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Rapid Environmental Organic Analysis by Direct
Sampling Glow Discharge Mass Spectrometry
and Ion Trap Mass Spectrometry:
Summary of Pilot Studies

FINAL REPORT

March 1990

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M. B. Wise, M. V. Buchanan, and M. R. Guerin

DOE Interagency Agreement No. 1769-A073-A1

Supported by
U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, Maryland 21010-5401

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EXECUTIVE SUMMARY

The purpose of this report is to summarize observations from pilot studies here to date which suggest that Direct Sampling Mass Spectrometry (DSMS) is a very promising technology for the rapid determination of organic pollutants in the environment and related samples. The term "direct sampling" is taken here to mean that the constituents of interest are introduced directly into the mass spectrometer with little to no sample preparation and without prior chromatographic separation. Glow Discharge Ionization Mass Spectrometry (GDMS) and Ion Trap Mass Spectrometry (ITMS) have been surveyed. GDMS studies have been carried out using an ionization source designed by the investigators and interfaced with a commercial quadrupole mass spectrometer. ITMS studies have been carried out using a commercial Finnigan ITMS modified according to the investigators' specifications. The ITMS is designed by the Finnigan Corporation as a research instrument and is not to be confused with its production model Ion Trap Detector (ITD) or the newer Ion Trap Spectrometer (ITS40).

Observations to date suggest that both technologies will be capable of quantitatively determining preselected organics in water, soil, and air samples at part per billion concentrations in less than five minutes. The approach appears immediately applicable to the determination of volatile organics, but studies suggest equal applicability to many semivolatiles using only slightly more complex sample-introduction methods. ITMS currently appears to be of generally broader applicability because of its ability to discriminate between isobaric constituents. Approaches for discriminating between such constituents and for identifying the presence of other interfering analytes are a part of our plans for subsequent research. Results of studies to date suggest many applications of immediate utility, however.

Progress reported here is predominantly a result of USATHAMA sponsorship. The Office of the Program Manager for Chemical Demilitarization (OMPCD) provided access to its ITMS and sponsored related work on the determination of airborne chemical agents. The National Cancer Institute Division of Chemical Carcinogenesis sponsored the work on the determination of ambient and urinary nicotine by ITMS and on tobacco smoke carcinogens. The Department of Energy Hazardous Waste and Remedial Actions Program has contributed funding for related capital equipment and is scheduled to co-fund environmental applications studies in fiscal year 1990. The U.S. Environmental Protection Agency Office of Solid Waste encouraged our evaluation of the applicability of ITMS to the determination of halocarbon solvents in waste oils and is considering funding a continuing effort in this and related areas.

The promise of DSMS for rapid environmental analysis is documented by the results summarized in this report and is supported by the interests of multiple federal agencies. A systematic evaluation of the technology for specific applications and for general applicability is to be initiated in fiscal year 1990 under USATHAMA leadership.

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INTRODUCTION

Mass spectrometry is often employed in the analysis of trace compounds due to its sensitivity and ability to characterize compounds with a high degree of confidence. For the analysis of mixtures, such as found in environmental samples, combined gas chromatography/mass spectrometry (GC/MS) is commonly employed. Using GC/MS, compounds in mixtures are separated using chromatographic methods prior to detection by the mass spectrometer. Unfortunately, in addition to the lengthy chromatographic step (typically an hour or more), environmental samples require one or more sample preparation steps to isolate the targeted compounds from the sample matrix. Thus, analysis of a water sample for volatile compounds requires an hour and sample preparation and analysis of semivolatiles in water requires eight hours. The time required for sample preparation and analysis results in costs between \$300 and \$1000 for the analysis of a single sample by standard GC/MS procedures for a single class of analytes. Thousands of these samples are analyzed each year, resulting in enormous costs. A method for more quickly analyzing these samples would reduce both the cost and time associated with these analyses.

In addition to a rapid means of quantitatively determining trace components in environmental samples, often prompt screening results are required. For example, in site remediation work, a rapid method for field screening of compounds would help to expedite critical engineering decisions. Presently, transporting samples to a central laboratory can require anywhere from a few hours (if a laboratory is located nearby) to several days or longer between the time the sample is taken and when laboratory results are available. Further, with a rapid and reliable screening method available, sites with no contamination could be quickly identified. This would result in fewer samples with no contamination being sent to a laboratory for full analysis, further reducing analytical costs.

Initial work conducted for USATHAMA centered on the investigation of glow discharge mass spectrometry for rapid analysis of trace organics in water and soil. This work was conducted using an idle Finnigan 3200 quadrupole mass spectrometer found in storage here at ORNL. Initial results using this 20 year old instrument modified with a cylindrical glow discharge source (described below) were extraordinarily promising. However, this instrument, due its small diameter (3/8 inch) quadrupole rods, analog detection electronics and line-of-site multiplier, could not attain the detection limits easily acquired with current mass spectrometers which have large diameter quadrupole rods, pulse counting digital electronics and off-axis multipliers. Initially, all data was collected manually and responses measured by manually measuring peak heights. During the course of the studies, a computer was interfaced to the Glow Discharge Mass Spectrometer (GDMS) and software was written to allow automated data acquisition and data manipulation.

Major problems were incurred with the electronics of the outdated Finnigan mass spectrometer, including failure of the RF oscillator and RF driver power supply. After several months experiencing additional difficulties in maintaining the instrument in operating condition and obtaining replacement parts from the vendor, approval was acquired to purchase components to upgrade the system to current state-of-the-art capabilities. New high sensitivity 3/4 inch diameter quadrupole rods, equipped with an axial ionizer and off-axis multiplier, and an electronics package was purchased from Extrel.

The off-axis multiplier should markedly increase the overall sensitivity of the instrument over line-of-sight detectors by reducing background noise arising from high energy neutrals, photons, and electrons. In addition, the new system allows the detection of negative ions, which will greatly enhance the detection of munitions compounds (which have highly electronegative nitro-substituents), as well as halogenated materials. A new vacuum chamber was constructed for this new instrument and the entire system was integrated into the pumping station from the old Finnigan 3200 instrument. This new system, which is currently in final stages of testing, will be used for future work on GDMS.

Work conducted for the Department of the Army (DA) Office of the Program Manager for Chemical Demilitarization (OPMCD) for the high sensitivity detection of chemical agents in air demonstrated the extraordinary detection limits (picograms and lower) obtainable with a new type of mass spectrometer based on a rf quadrupole trapped ion device. This instrument, an ion trap mass spectrometer (ITMS), is described in detail in the section on ITMS. In addition, this instrument operates at much higher pressure than conventional mass spectrometers (10^{-3} to 10^{-4} torr versus 10^{-6} , respectively). This allows a higher flow (sampling rate) to be introduced into the instrument, which is necessary for direct sampling of materials purged from solution.

While the GDMS instrument was down and the shipment of the new components was awaited, pilot studies conducted using the OPMCD ITMS demonstrated the potential for rapidly analyzing environmental samples by purging water and soil samples directly into the ITMS. The ITMS also offers the advantage of being able to analyze mixtures more readily than a single quadrupole instrument because of its ability to operate as a tandem mass spectrometer (MS/MS). Due to the high potential demonstrated in these pilot studies, an ITMS has been purchased for further studies. The instrument was installed and met specifications in late November 1989.

This report serves as a summary of scoping studies performed at ORNL since April 1988. Primary attention has been given to the analysis of volatiles in water, however studies have also been conducted on volatiles in soil and semivolatiles in water. Work to date has shown that both GDMS and direct sampling ITMS possess exceptional promise for the determination of trace organics in both water and soil in a few minutes instead of hours, with little or no sample preparation steps. As a result, these techniques allow high sample throughput, even as high as 10 or more samples per hour. In addition, these technologies show potential for development into field-portable devices.

The following report is divided into two sections, corresponding to experiments conducted with glow discharge mass spectrometry and direct sampling ion trap mass spectrometry.

GLOW DISCHARGE MASS SPECTROMETRY

Our earlier work for USATHAMA (and later, OPMCD) led to the development of a glow discharge ionization source designed specifically for the rapid (< 15 sec) detection of trace chemical agents in air. The compounds which these studies were directed toward included GB, VX and HD, although work here at ORNL was restricted to the study of

agent simulants. A schematic of the glow discharge source is shown in Figure 1. The source, which consists of a pair of concentric cylindrical electrodes, an ion extraction lens, and an ion focusing lens, is mounted on a 2.75 inch diameter conflat flange, which also supports feedthroughs for electrical connections. The two discharge electrodes (one being cylindrical and the other being a concentrically placed wire) are separated by about 0.5 cm, giving a total discharge volume of about 2 cm³. All gas entering the ion source passes through the cylindrical discharge region, which results in high ionization efficiency, which in turn yields high sensitivity detection of analytes. Air enters the source through a 1/4 inch OD stainless steel tube mounted on the flange and air flow is regulated using a needle metering valve. The entire source is housed in a vacuum chamber, shown schematically in Figure 2. A 1.5 mm orifice separates the ion source region from the quadrupole mass analyzer region, allowing the analyzer to be maintained at required pressures of 10⁻⁶ torr while the source is operated at pressures of 200 to 300 torr.

The ion source is operated by applying a potential of about -400 volts DC to the outer discharge electrode and +100 volts DC to the inner discharge electrode. Using laboratory air as the discharge gas at a source pressure of 250 mTorr, the discharge current was typically 5 to 10 mA. The ion focussing lens is typically set at +100 volts. The ion extraction lens may be adjusted from -1 to -50 volts. At low potentials spectra arise from proton transfer chemical ionization reactions, yielding predominately protonated molecular ions at one mass higher than the molecular weight of the molecule, (M + H)⁺. At higher extraction levels, more fragmentation occurs, yielding spectra more similar to electron ionization.

A unique feature of the glow discharge source is the ability to introduce relatively large (2 mL per sec) flows of air into the mass spectrometer without degradation of performance of either the discharge source or the mass spectrometer. Background spectra of laboratory air saturated with water run in the chemical ionization mode, where the ion extraction lens was held at low potentials, is shown in Figure 3. A spectrum of the same background obtained in the fragmentation mode, where the lens was kept at higher potentials, is shown in Figure 4. Note that even using water-saturated air that little interference from water cluster ions is observed, e.g., no clusters are observed above H₃O(H₂O)₂⁺, which is of very low abundance.

Using the Finnigan 3200 analog detection quadrupole mass spectrometer outfitted with the glow discharge source, 50 parts-per-trillion of dimethylmethylphosphonate (DMMP) could be detected in air in real time. Better detection limits could have certainly been obtained with modern mass spectrometers which employ larger diameter quadrupole rods, pulse counting detection and off-axis multipliers.

Volatiles in Water

The studies with chemical agent simulants demonstrated that introducing large volumes of air saturated with water into the GDMS yielded no ill-effects on the instrument. These results suggested that GDMS might be applicable to the rapid analysis of volatile materials in water and soil. A simple sample interface was designed using a 25 mL VOA vial, 2 hole rubber stopper, and 1/4 inch teflon transfer lines (Figure 5). Laboratory air was drawn through the vial and into the GDMS, where it swept volatiles in the headspace

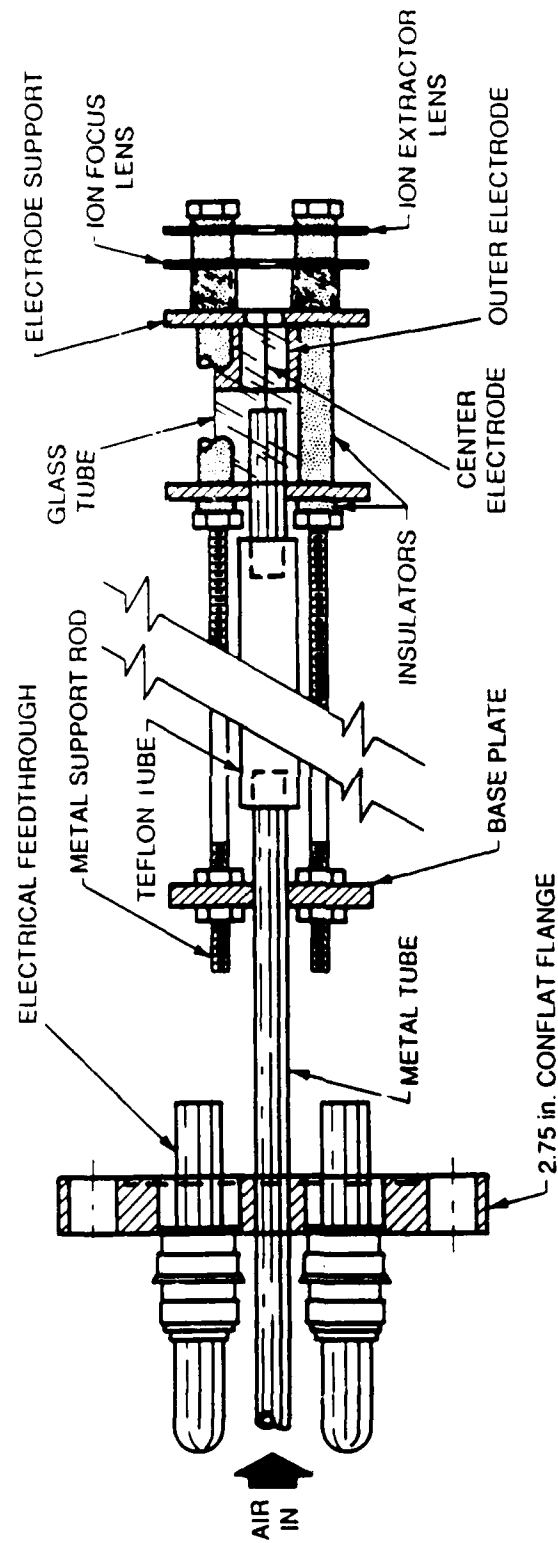


Figure 1. Glow Discharge Ionization Source

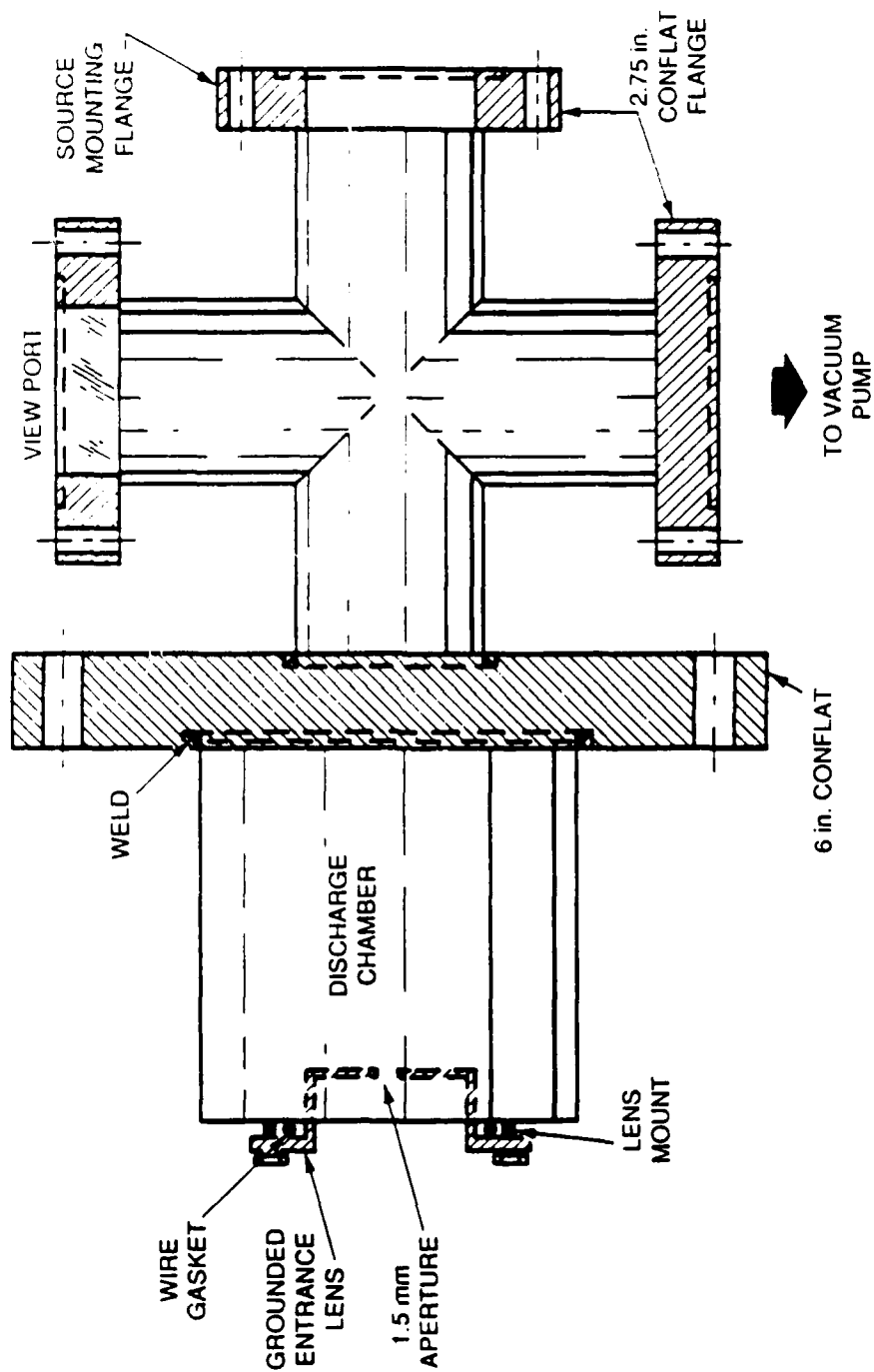


Figure 2. Glow Discharge Source Vacuum Chamber

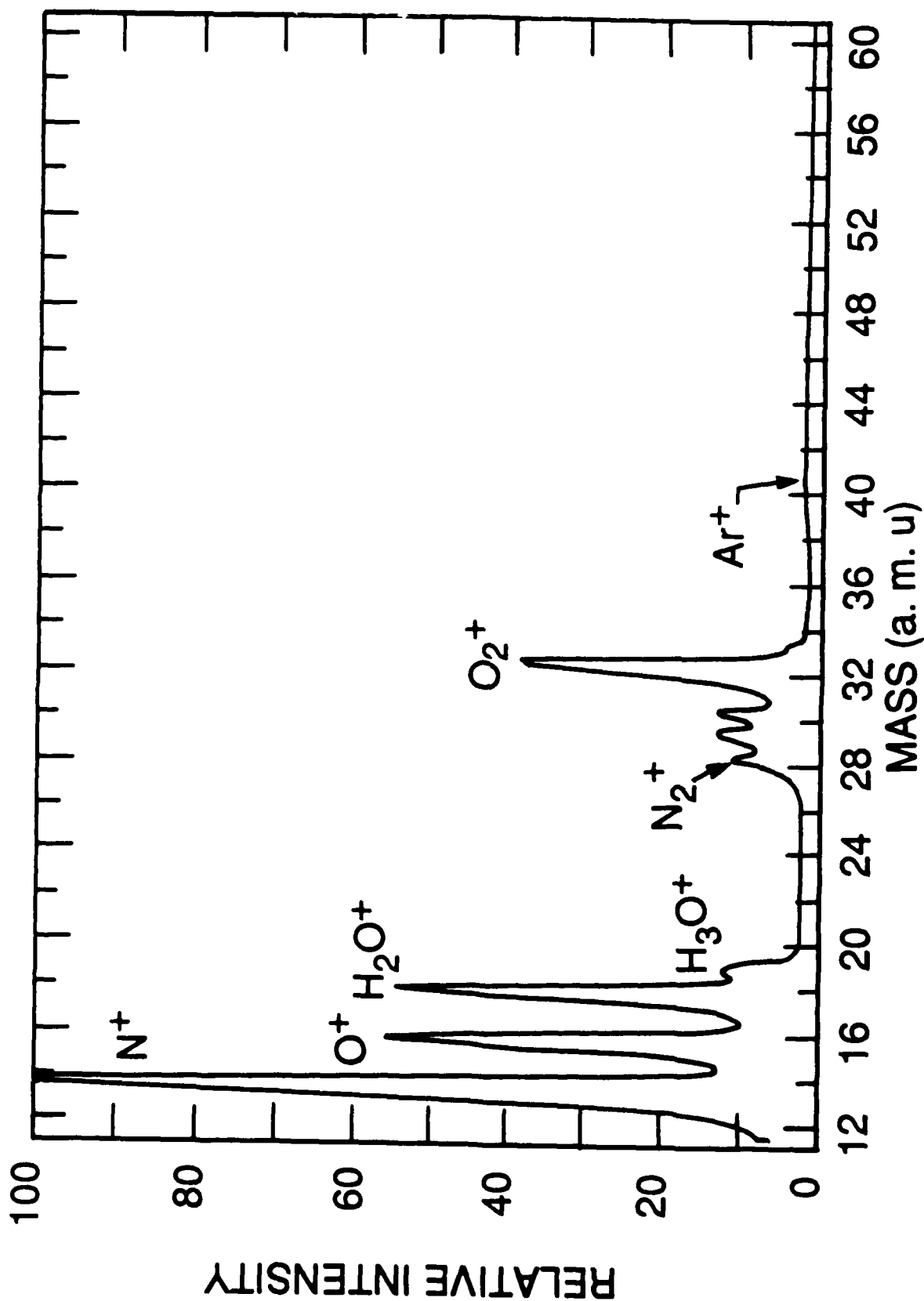


Figure 3. Background Air: Fragmentation Conditions

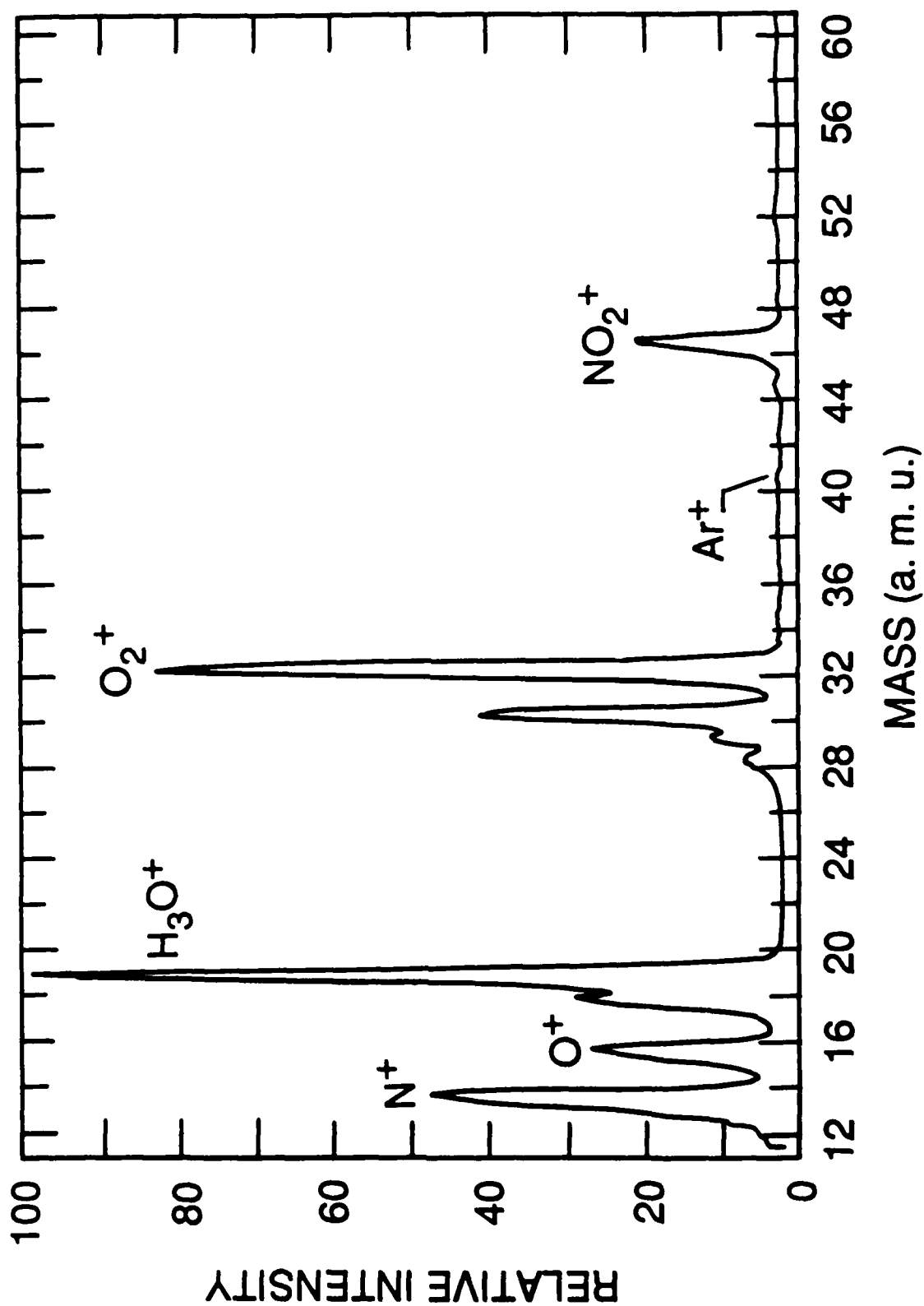


Figure 4. Background Air: Protonation Conditions

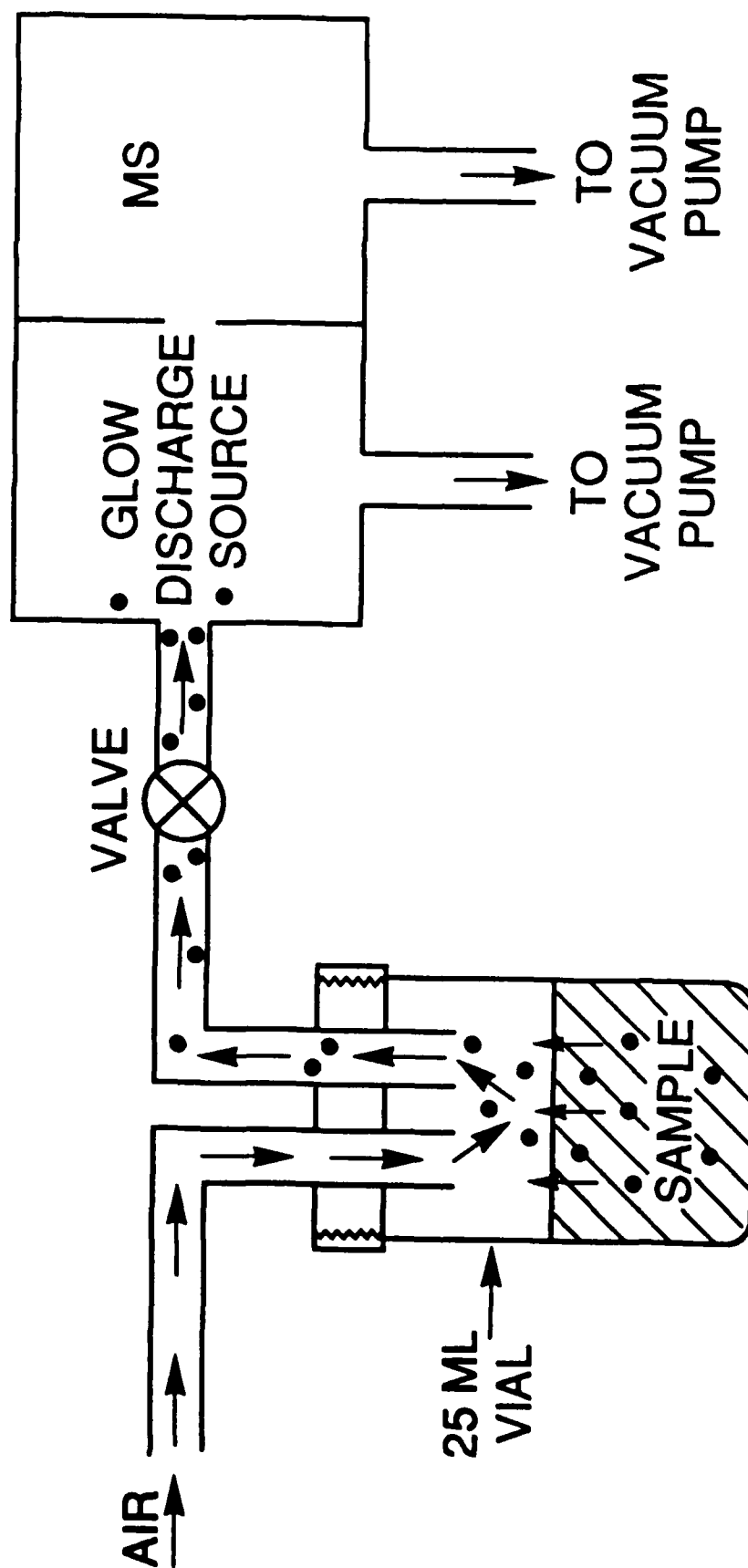


Figure 5. Glow Discharge Sample Inlet for Headspace Analysis

over the water into the GDMS source. Figure 6 illustrates the typical response observed in monitoring the headspace over an aqueous solution containing 88 parts-per-billion (ppb) benzene. In this spectrum, the instrument was repeatedly scanned over masses 78 and 79, corresponding to the molecular ion and protonated molecular ion of benzene, respectively. The intensity of the detected ions was observed to increase initially and then decrease slowly over about a 30 minute period (in this particular spectrum, the sample was removed after 10 minutes to demonstrate the absence of any "memory" effects). Quantitation was performed by measuring the average peak height between 2 and 4 minutes, when the response had leveled. A series of solutions ranging in concentration from 10 to 90 ppb were run, and as shown in Figure 7, the response was observed to be linear (correlation coefficient of 0.998). An unknown was prepared by laboratory personnel working on the USATHAMA/EPA Holding Time Study, which contained benzene as well as sixteen other volatile organics. The concentration of benzene was determined to be 55 ppb using the GDMS, compared to a value of 55.5 ppb determined independently by EPA protocols using GC/MS. Note, however, that the total analysis time using the GDMS was a few minutes, rather than over an hour required for the conventional purge and trap GC/MS method.

Instead of monitoring the headspace over a sample, volatiles may also be purged from an aqueous solution for subsequent analysis. It was determined that an improvement in the signal to noise ratio and a faster response could be achieved by lowering the air inlet tube (shown in Figure 5) below the solution level to the bottom of the VOA vial, allowing the volatile materials to be purged from the water. Subsequently, an improved sampling device was constructed. A screw cap and teflon coated silicon cap liner were placed on either side of a stainless steel disk and were used to seal the purge vessel. Two 1/16" stainless steel tubes were welded through this disk, with the longer tube (extending to near the bottom of the purge vessel) serving as an inlet for the purge gas (laboratory air). A shorter tube (flush with the disk) served as a means of transferring the purged materials into the GDMS.

As shown in Figure 8, which as in Figure 6 is a sample of 88 ppb benzene in water, the signal increased initially, but then decreased more rapidly than with headspace monitoring. Depending upon the flow rate used, purge times were typically less than two minutes per sample. The signal was integrated for two minutes and this was used for quantitation. The detection limits were less than the lowest measured concentrations of 8.8 ppb for benzene, 5.5 ppb for trichloroethylene, and 10 ppb for tetrachloroethylene with a signal-to-noise ratio of at least 10:1 demonstrated at these levels for each compound. A calibration curve for trichloroethylene in water at levels between 5 and 55 ppb is shown in Figure 9, which illustrates the linearity of response. In general, at concentrations of 100 ppb replicates were measured with relative errors $[(\text{observed}-\text{actual})/\text{actual}]$ of about 1 to 5% (95% confidence limit). The relative error increased to about 5 to 10% at 50 ppb, and 15-20% at levels less than 10 ppb. It should be noted again that the performance of the GDMS was not degraded by the presence of high quantities of water from the sample or air used as purge gas. In fact, upon several occasions, water from the sample was accidentally introduced into the GDMS, but the instrument recovered in the matter of a few minutes with no ill effects.

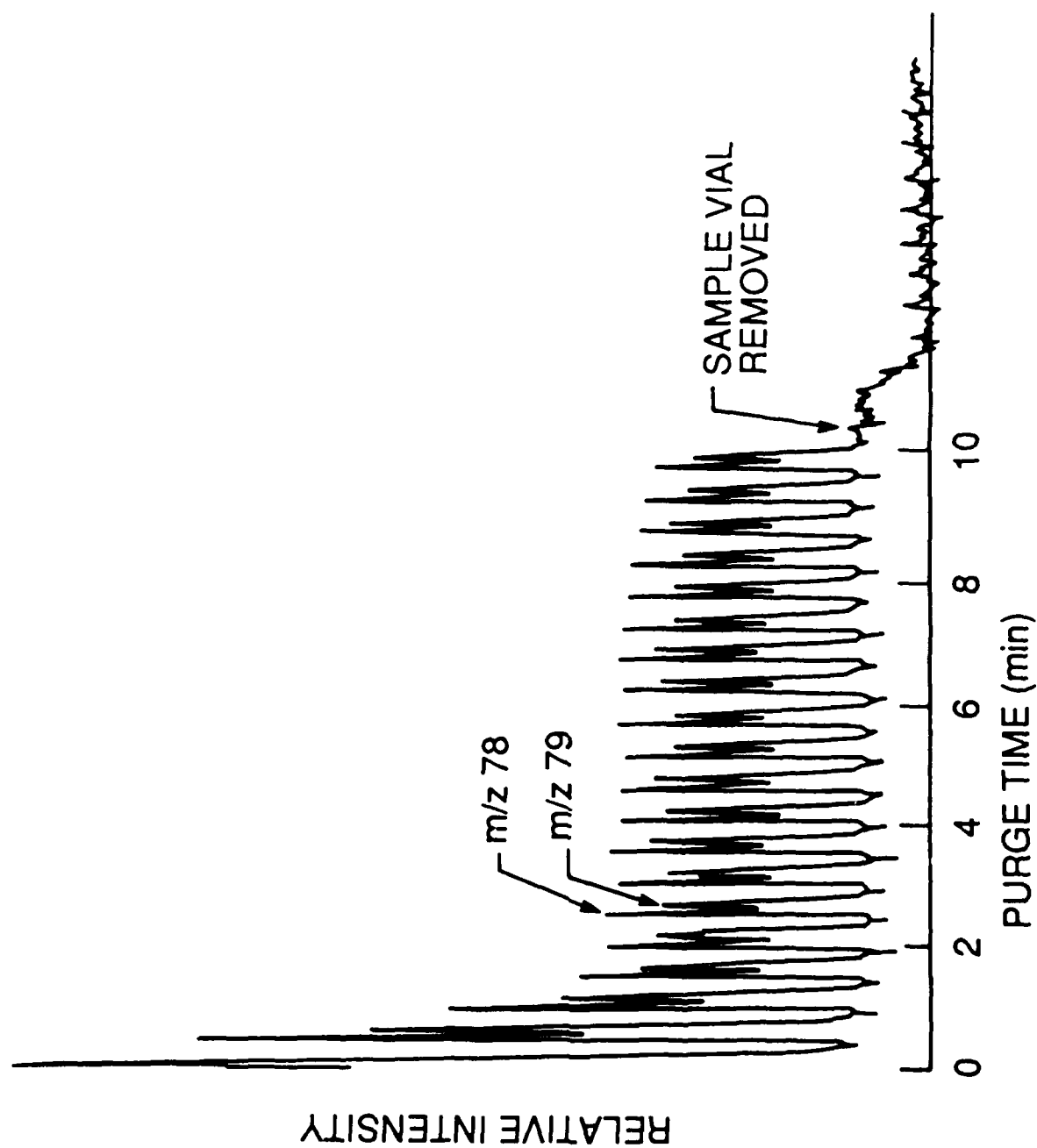


Figure 6. 88 ppb Benzene in Water, Headspace Analysis, Repeated Scans of m/z 78 and 79

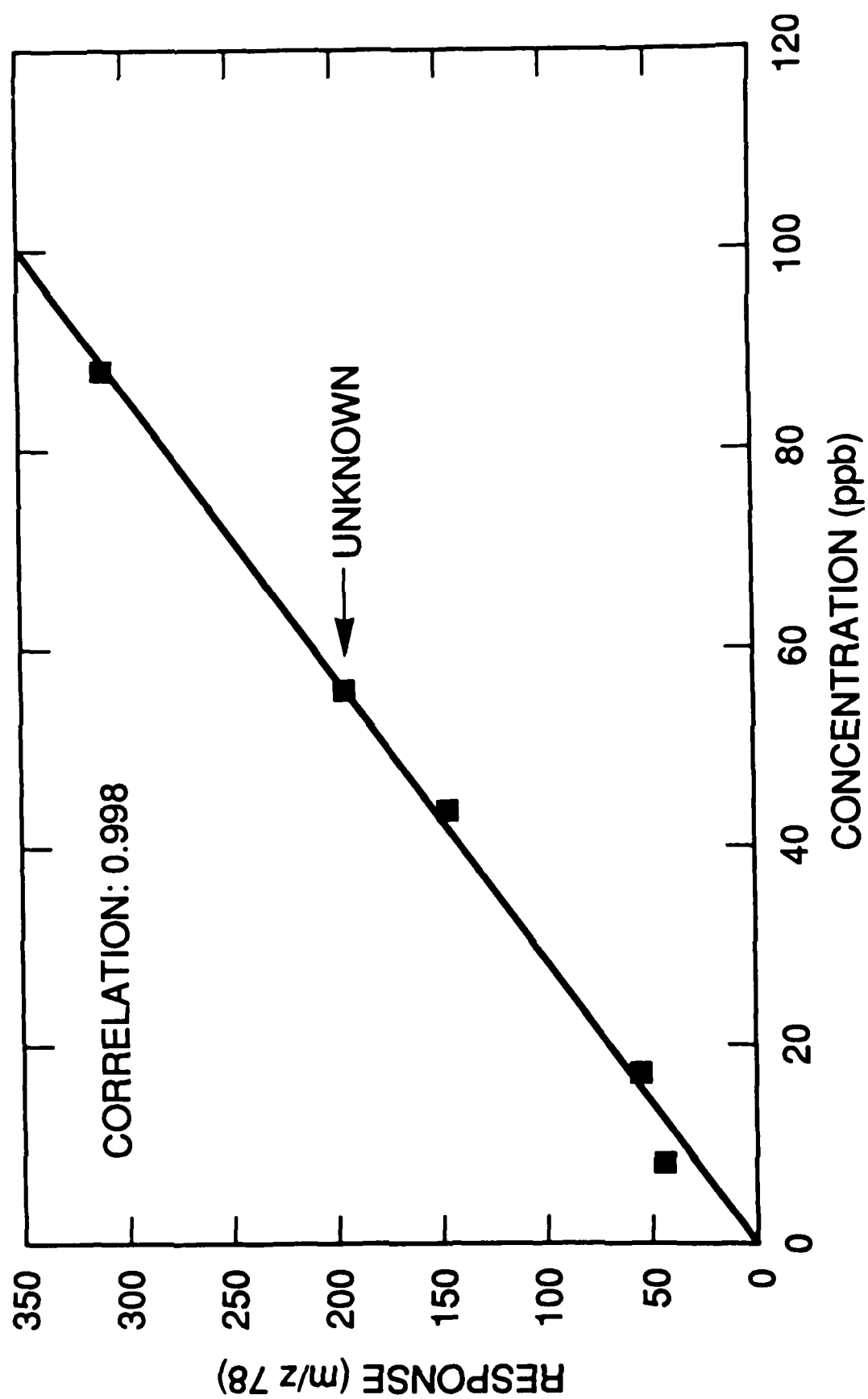
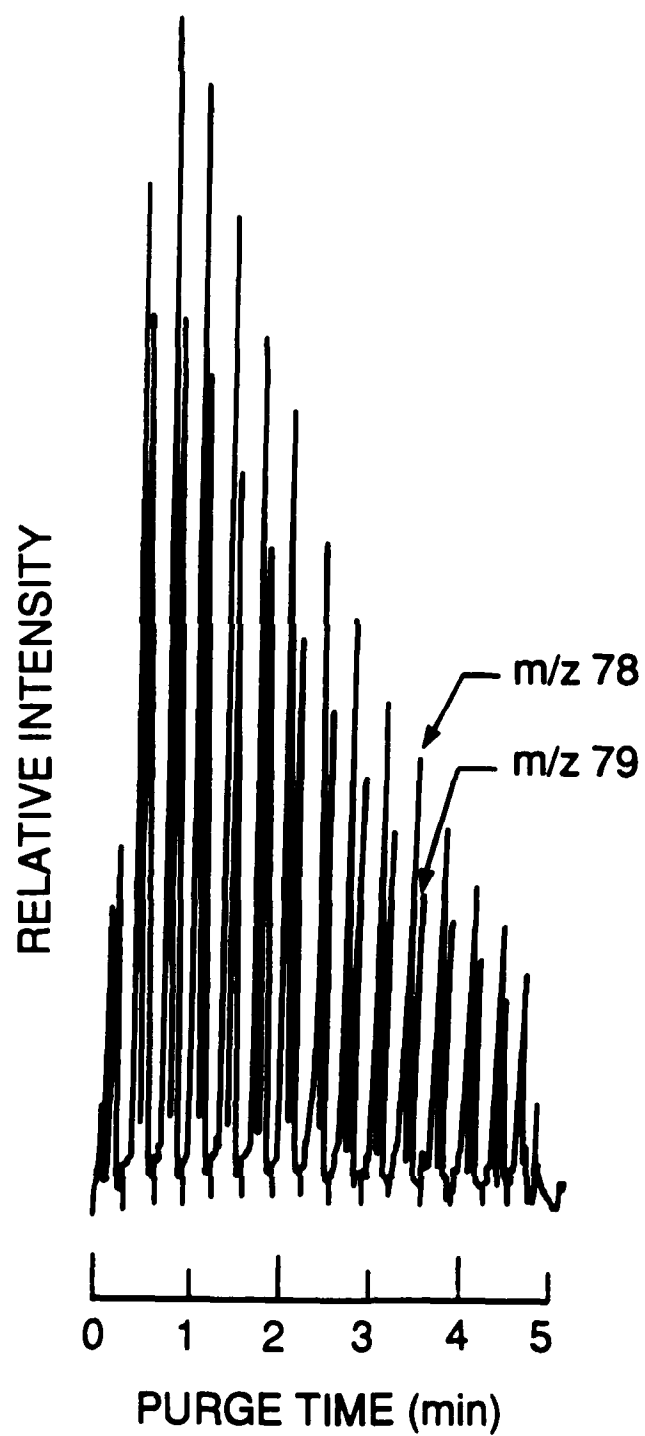


Figure 7. Benzene in Water - Headspace Monitoring

Figure 8. 88 ppb Benzene in Water, Solution Purge,
Repeated Scans of m/z 78 and 79



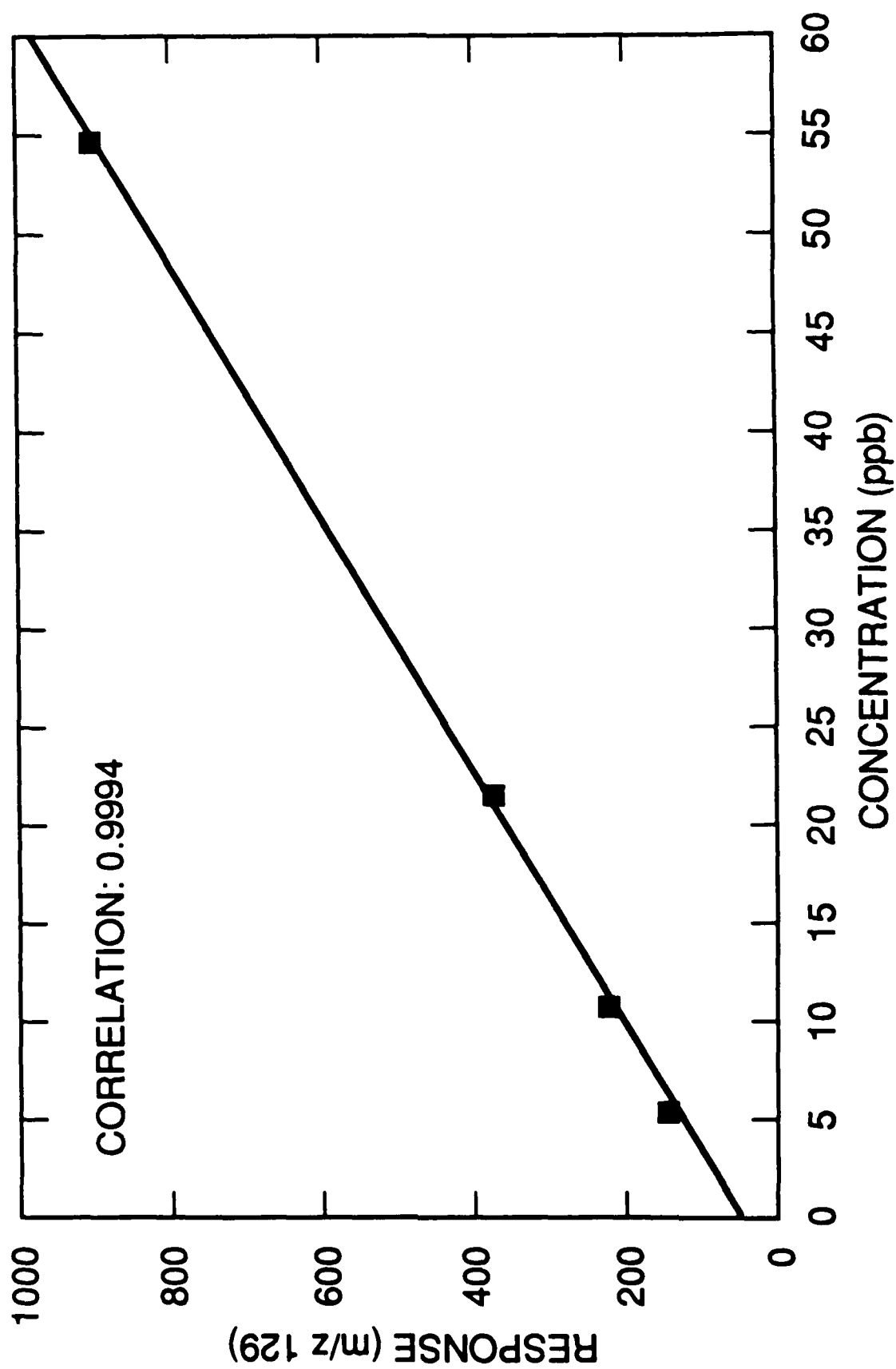


Figure 9. Trichloroethylene in Water - Solution Purge

As an example of the application of GDMS, Figure 10 illustrates the response for chloroform in tap water. The distinctive signal for chloroform with M^+ ions at m/z 83 and 85 (arising from chlorine isotopes) is readily observed. The levels of chloroform were measured at 10 to 20 ppb by GC/MS, however, the analysis required about an hour.

Mixtures of benzene (molecular weight 78), trichloroethylene (mw 132), and tetrachloroethylene (mw 164) were examined to evaluate the effectiveness of GDMS for the analysis of mixtures. In this case, the instrument was scanned from m/z 75 to 170. No problems were encountered in observing all three compounds at concentrations between 10 and 100 ppb. However, none of these compounds give spectra which interfere with the other compounds. In real samples where many compounds are present, the probability of spectral interferences is great; however, tandem mass spectrometry (MS/MS) can be employed to discriminate against possible interferences. This would require the use of a triple quadrupole instrument (QQQ) or another instrument capable to perform these types of selective MS/MS experiments, such as the ITMS, which is discussed later.

Volatiles in Soil

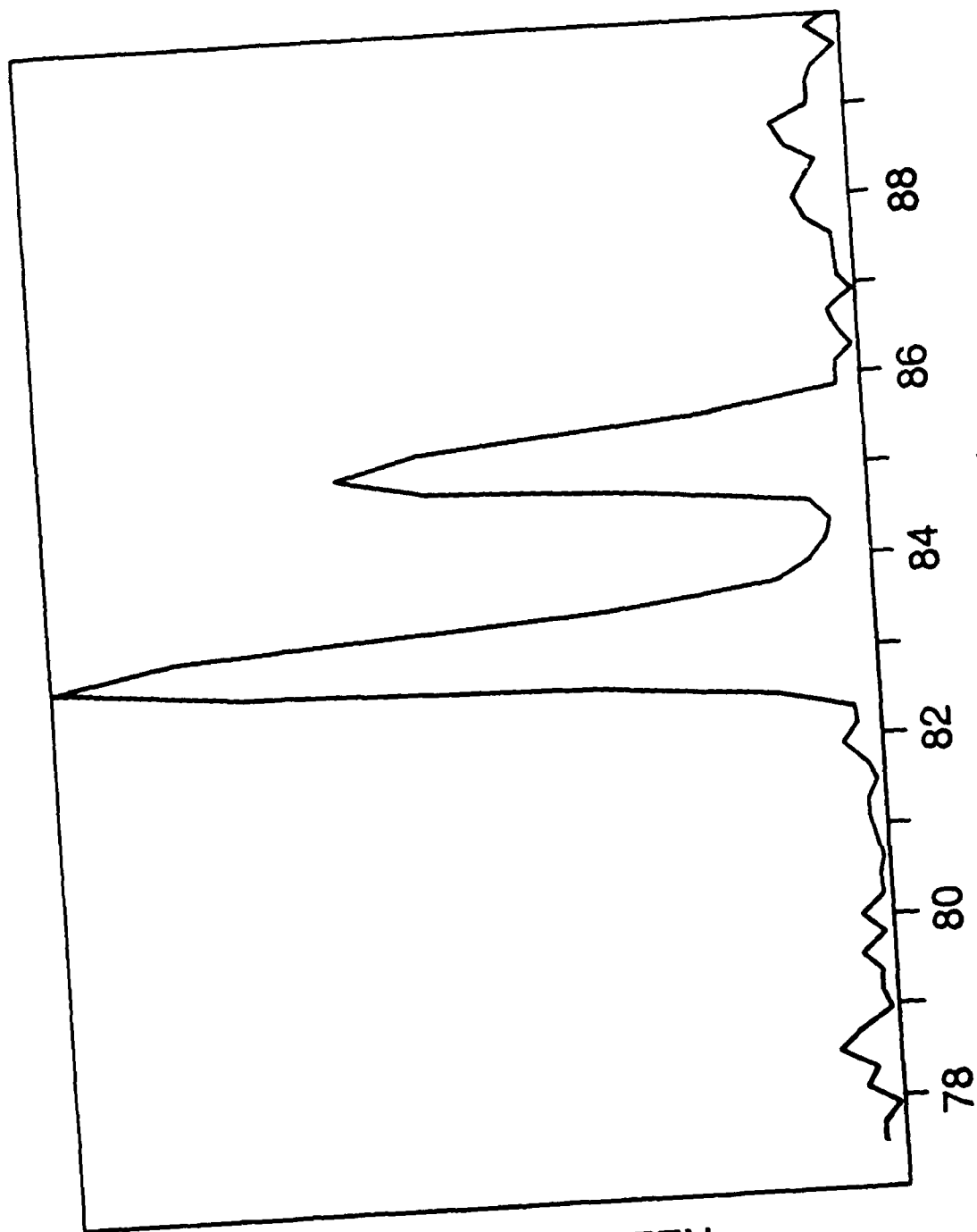
Volatile compounds in soils may be analyzed in a similar manner by making aqueous slurries prior to purging. For example, 10 mL of water was added to 5 g of soil spiked with ppb levels of benzene. The solution was stirred slowly for two minutes in a capped VOA vial and then purged directly into the GDMS. In Figure 11, a calibration curve is shown with benzene levels between 20 and 160 ppb in soil and three replicates at each concentration. As can be seen from this curve, reproducibility and linearity are very good. Lack of fit parameters are included in Appendix I. Four replicates of a blind soil sample spiked with benzene (prepared by personnel working in the USATHAMA/EPA Holding Time Study) were run using this methodology. The level of benzene in this sample was determined to be 57 ppb. This compared with an actual value of 60 ppb. Total analysis time was 5 minutes per sample, as compared to an hour for conventional purge and trap GC/MS.

Semivolatiles in Water

The utility of GDMS for the analysis of semivolatiles in water was also briefly investigated. In these studies, the temperature and pH of the solutions were altered to enhance the purging of semivolatiles from water. Solutions of phenol in water were tested under various temperature conditions, including room temperature (about 25°), 40°, and 60°C. Also, citric acid was added to some solutions to lower the pH to 2 to observe the effect of pH on the purgability of phenol. Ions observed were m/z 94, corresponding to M^+ , and m/z 95, corresponding to $(M + H)^+$. It was observed that at pH 2 and temperature 60°C, phenol could be observed at levels of less than 5 ppm, as shown in Figure 12. The actual detection limit for phenol under these conditions is probably a factor of 5 to 10 lower than this. The signal at m/z 91 was determined to arise from the methanol used in the preparation of the phenol stock solution from which the sample solutions are made. Solutions made without methanol did not exhibit this peak.

Experiments were also conducted with 2,4-dinitrophenol, a compound of interest to USATHAMA. These tests indicated that this material is very difficult to purge from

RELATIVE INTENSITY



MASS (a. m. u.)

Figure 10. MS of Chloroform in Water (~ 10 ppb) - Glow Discharge, Solution Purge

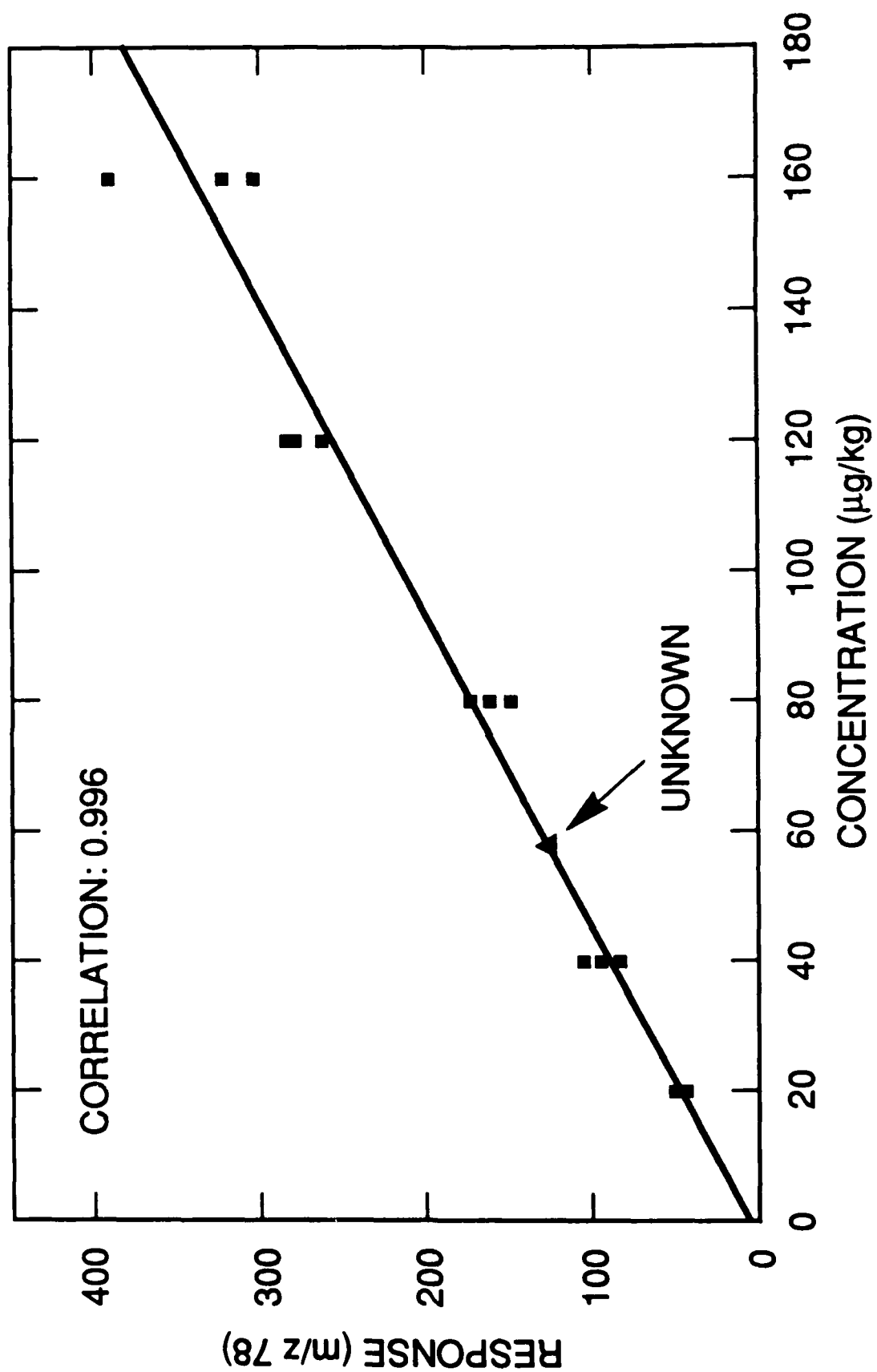


Figure 11. Benzene in Soil - Slurry Purge

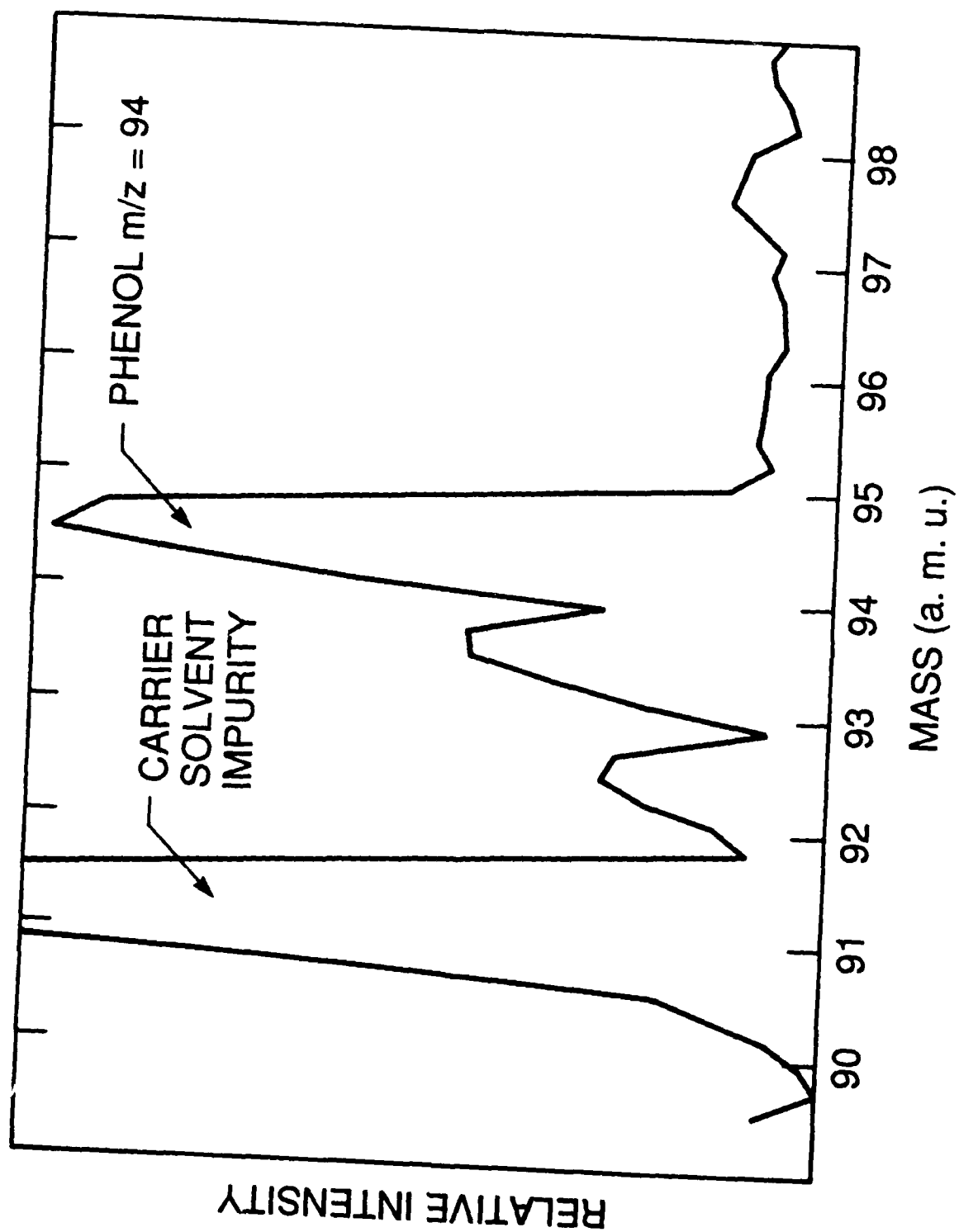


Figure 12. MS of 5 ppm Phenol in Heated Water (60°C, pH2) - Glow Discharge Solution Purge

water even when the solution was heated to 60°C and the transfer lines into the GDMS were heated. Heating the solution to higher temperatures resulted in too much water being introduced into the instrument, causing difficulties with the ion source discharge. As described in the next section, thermal desorption from resin beds or glass wool promises to be an effective means of determining semivolatiles. Other approaches are also being considered.

DIRECT SAMPLING ION TRAP MASS SPECTROMETRY (ITMS)

As mentioned previously, work for the DA Office of the Program Manager for Chemical Demilitarization for involving rapid detection of chemical agent simulants (and more recently actual chemical agents) trapped on air sampling resins demonstrated the ability of ITMS to detect trace levels (picograms and lower) of compounds and to handle relatively large gas flows (100 mL/min). It was therefore believed that the ITMS might be amenable to the direct introduction of materials purged from water and soil solutions, as was done with the GDMS. These experiments were conducted using a Finnigan ITMS with the standard open/split capillary GC interface and specially equipped with two 330 L/s air cooled turbomolecular pumps and an electropolished vacuum chamber. The open/split GC interface was used to introduce the samples directly to the ITMS.

Under normal operating conditions, helium pressures of 10^{-3} to 10^{-4} torr are required in the ITMS cell to stabilize the trajectories of the ions in the cell. For this reason, helium was used as the purge gas for the introduction of the volatiles into the ITMS, as shown in Figure 13. The sampling device used in the GDMS system was used for the ITMS studies. The effluent line from the sampling device was connected to a tee, with one leg of the tee joined to the open split interface of the ITMS and the second leg connected to a needle valve. This valve can be adjusted to change the flow into the ITMS transfer line.

Helium flow into the sampling device was approximately 20 to 100 mL/min. The open/split interface admitted a flow of approximately 0.5 mL/min into the ITMS. This means that typically only between 1 and 5% of material sampled is admitted into the ITMS with the remainder being vented. The detection limits listed below might be reduced if the split going into the ITMS were increased. In these initial studies, this was not attempted. However, it should be noted that a resin trap can be placed on the split vent line to trap the material being purged. This trap could be archived for analysis by standard methods at a later date and would represent the exact sample analyzed by the ITMS. Tests conducted by members of the Special Projects Group of our Section with triple sorbent traps containing Tenax, Carbotrap, and Ambersorb XE-340 have shown that at flow rates of 40 mL/min, breakthrough of even very volatile compounds, such as 1,1-dichloroethene (DCE), is negligible. Even at flows of 250 mL/min, breakthrough for DCE increases only to about 20%. Thus, using a sorbent trap represents a viable means of capturing these volatile materials for analysis at a later time. This feature would be especially desirable when the ITMS is used as a screening method.

In many of the experiments described below, water in the purged material was ionized to form H_3O^+ , which in turn ionized the analyte molecule by transfer of a proton to form

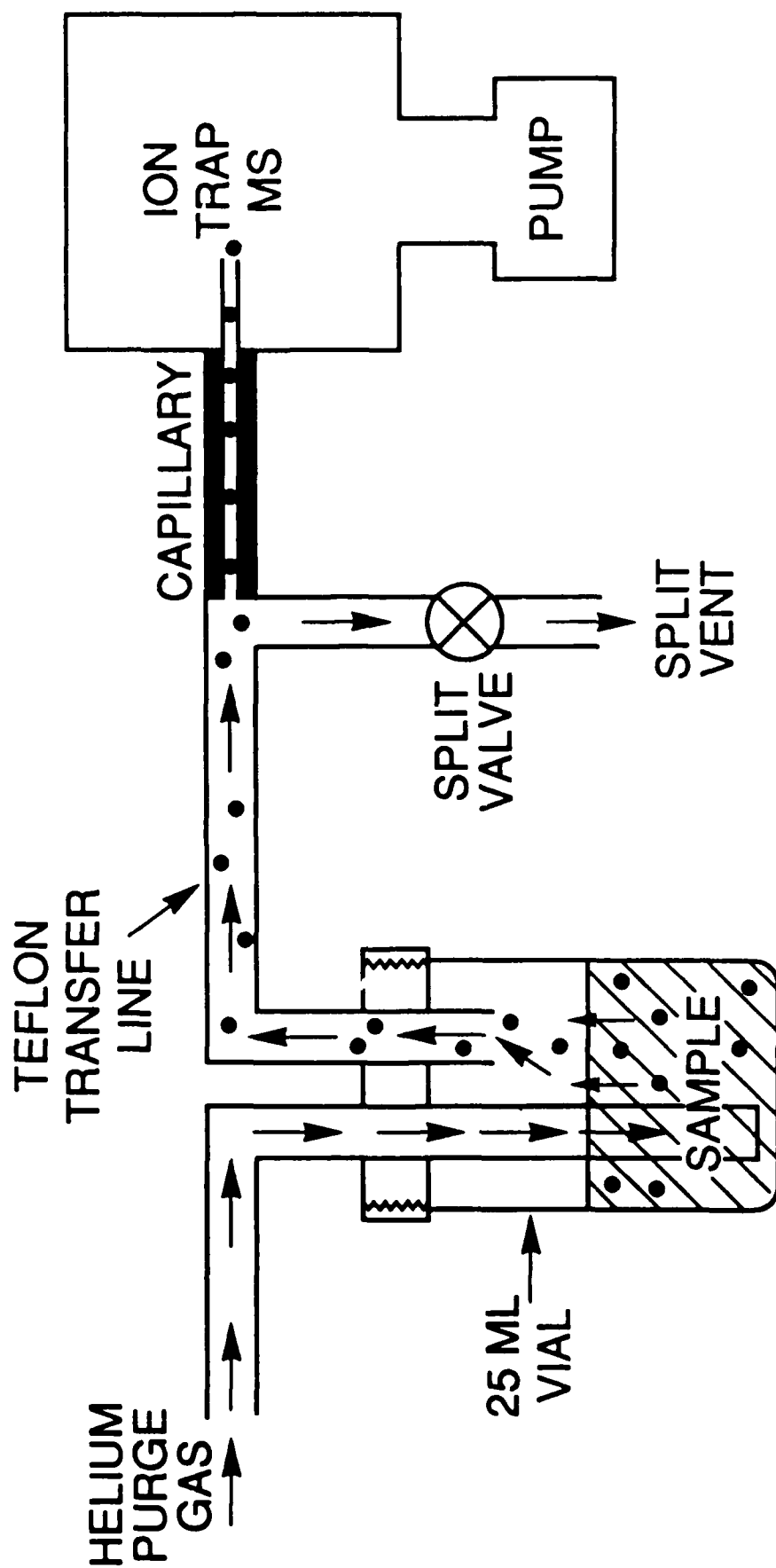


Figure 13. ITMS Sample Inlet

$(M + H)^+$. By altering the conditions (via a simple computer command) in the ITMS, one may also obtain conventional electron ionization spectra, even with significant levels of water present, as shown in Figure 14. This spectrum, resulting from purging a solution containing 100 ppb benzene in water, exhibits an M^+ ion at m/z 78 and its normal isotope peak at m/z 79, instead of the $(M + H)^+$ peak obtained under chemical ionization conditions. Charge transfer reactions, as well as selective chemical ionization using proton transfer reagents other than water, may also be employed with the ITMS. Both positive and negative ion spectra may be obtained on an ITMS; however, to this point only positive ion spectra have been used in these studies.

Volatiles in Water

Initial experiments were conducted with solutions of benzene in water. Figure 15 shows the purge profile of 10 ppb of benzene obtained under water chemical ionization single stage MS conditions. Spectra were taken by scanning from m/z 50 to 200 and yielded $(M + H)^+$ ions at m/z 79. The purge profile represents the total ion current as a function of time. The integrated ion current over a specified purge period, typically two minutes, is used for quantitative measurements. The purge profile will change due to flow rate and sample matrix (see discussion on oils below); however, reproducible purge profiles are obtained when all solutions, including standards and samples, are purged under similar conditions.

Standards of benzene in water having concentrations of 1, 10, 50 and 100 ppb were prepared and measurements at each concentration were made in triplicate. The purge of the material from solution was completed in a few minutes and the resulting purge profiles were integrated. The response, as shown in Figure 16, was observed to be linear over this concentration range (correlation coefficient of 0.9998). Relative error (at the 95% confidence interval) ranged from 5% at 100 ppb to 20% at 1 ppb. Lack of fit parameters are provided in Appendix I. It should be noted that detection limits for benzene below 1 ppb should be obtainable using direct sampling ITMS with only minor modifications to the sampling apparatus and/or analyzer configuration. These modifications were not attempted with the OPMCD instrument. However, using the MS/MS capabilities of the ITMS, spectra were obtained for a solution containing less than 500 parts-per-trillion benzene, as shown in Figure 17. In this daughter ion spectrum, the transition for the m/z 79 ion (arising from water chemical ionization of benzene) to m/z 77 was observed. The ion at m/z 95 probably arises from a reaction with water.

Further investigations have shown that direct sampling ITMS is readily applicable to the analysis of a variety of other volatiles in water, including toluene, trichloroethylene, tetrachloroethylene, methylene chloride, chloroform, dichloroethane, vinyl chloride, and bromomethane at levels between 1 and 200 ppb. Detection limits for these compounds are generally at 1 ppb, although, as noted above, simple modifications could improve these detection limits. All of these compounds gave linear calibration curves with correlation coefficients of 0.99 or better and reproducibility ranging from about 5 to 15% (at the 95% confidence level). Lack of fit parameters for each of these compounds are included in Appendix I.

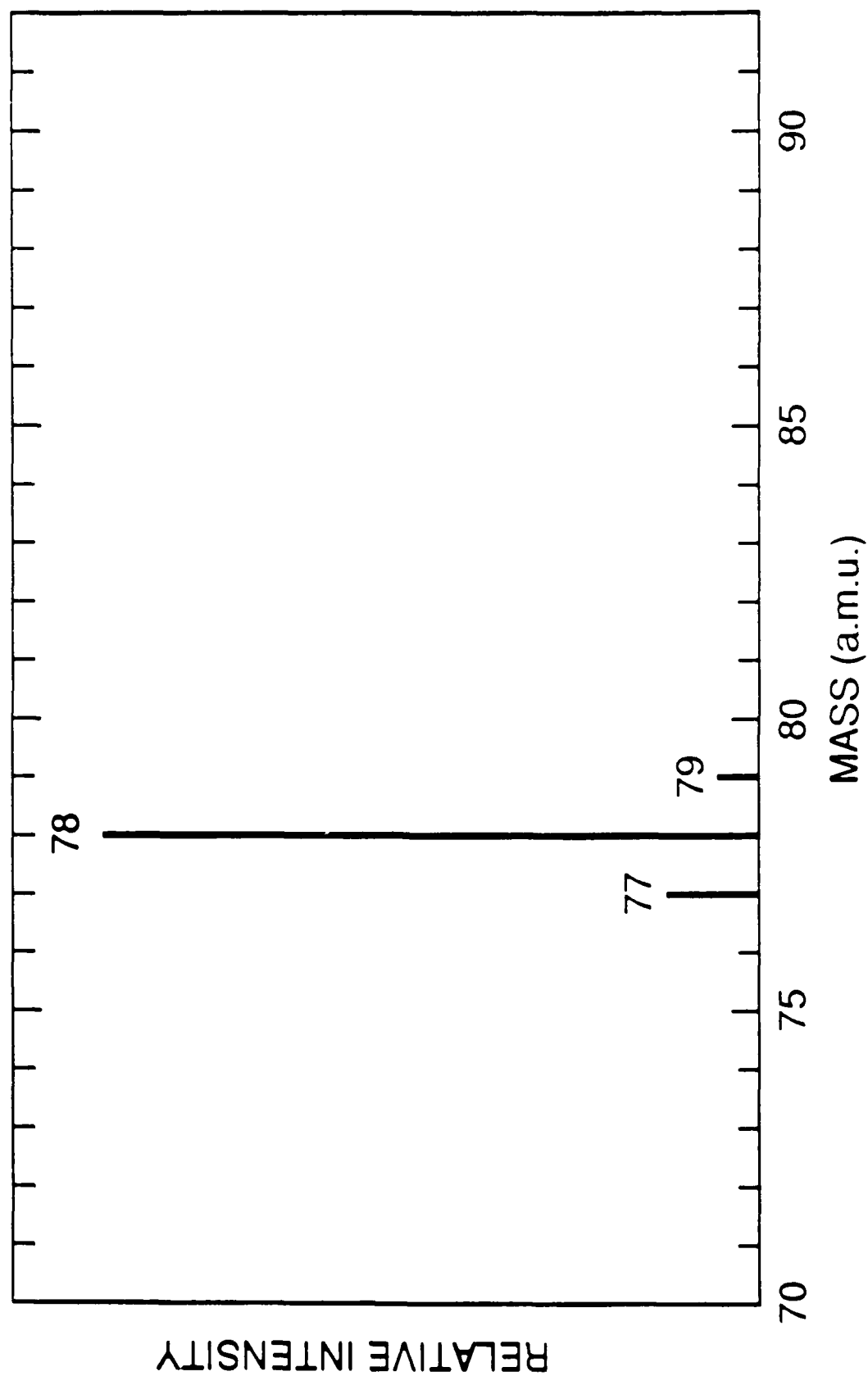


Figure 14. MS of 100 ppb Benzene in Water, Solution Purge, Ion Trap MS Electron Impact Conditions

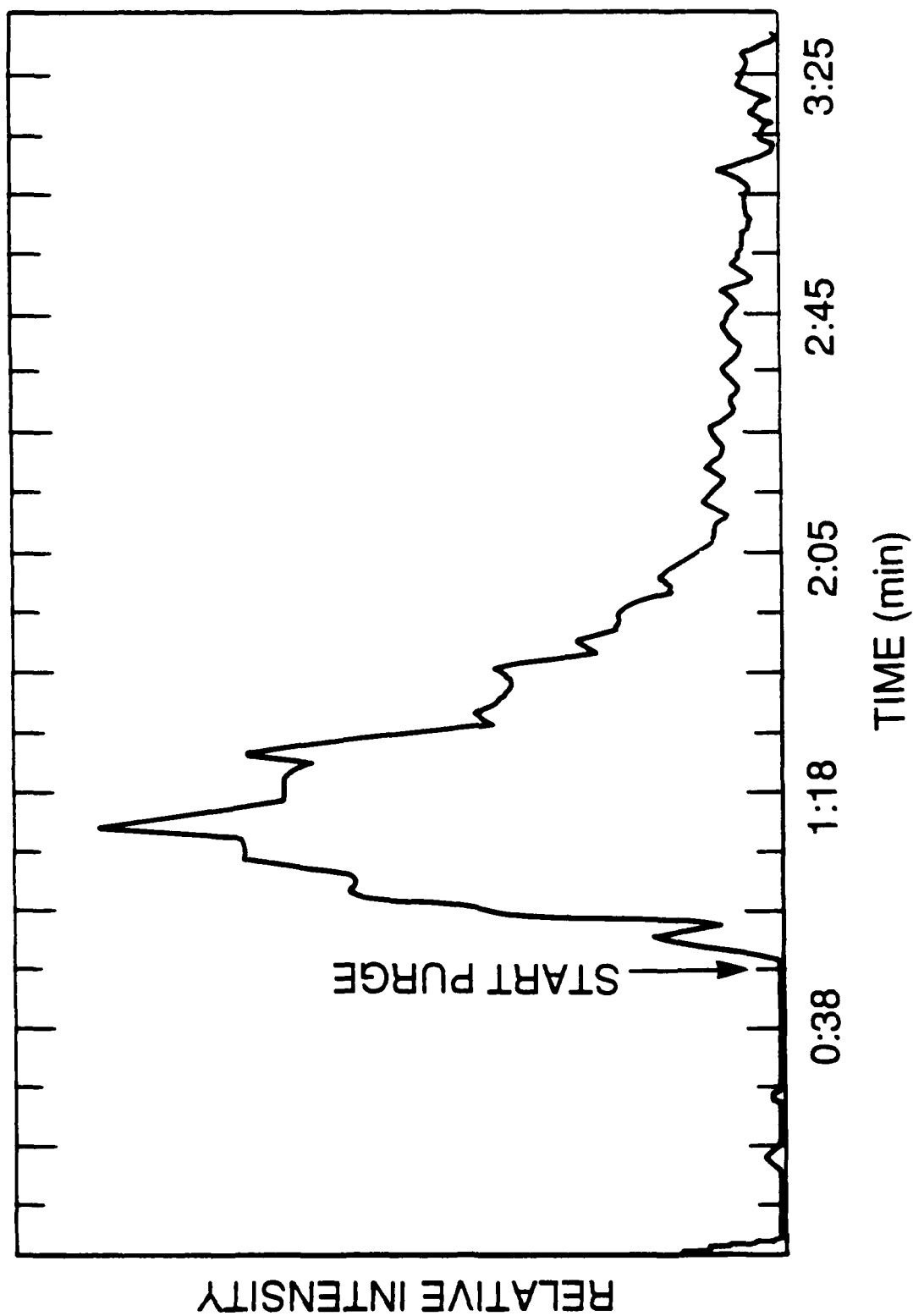


Figure 15. Purge Profile of 100 ppb of Benzene in Water, Solution Purge, ITMS Water Chemical Ionization

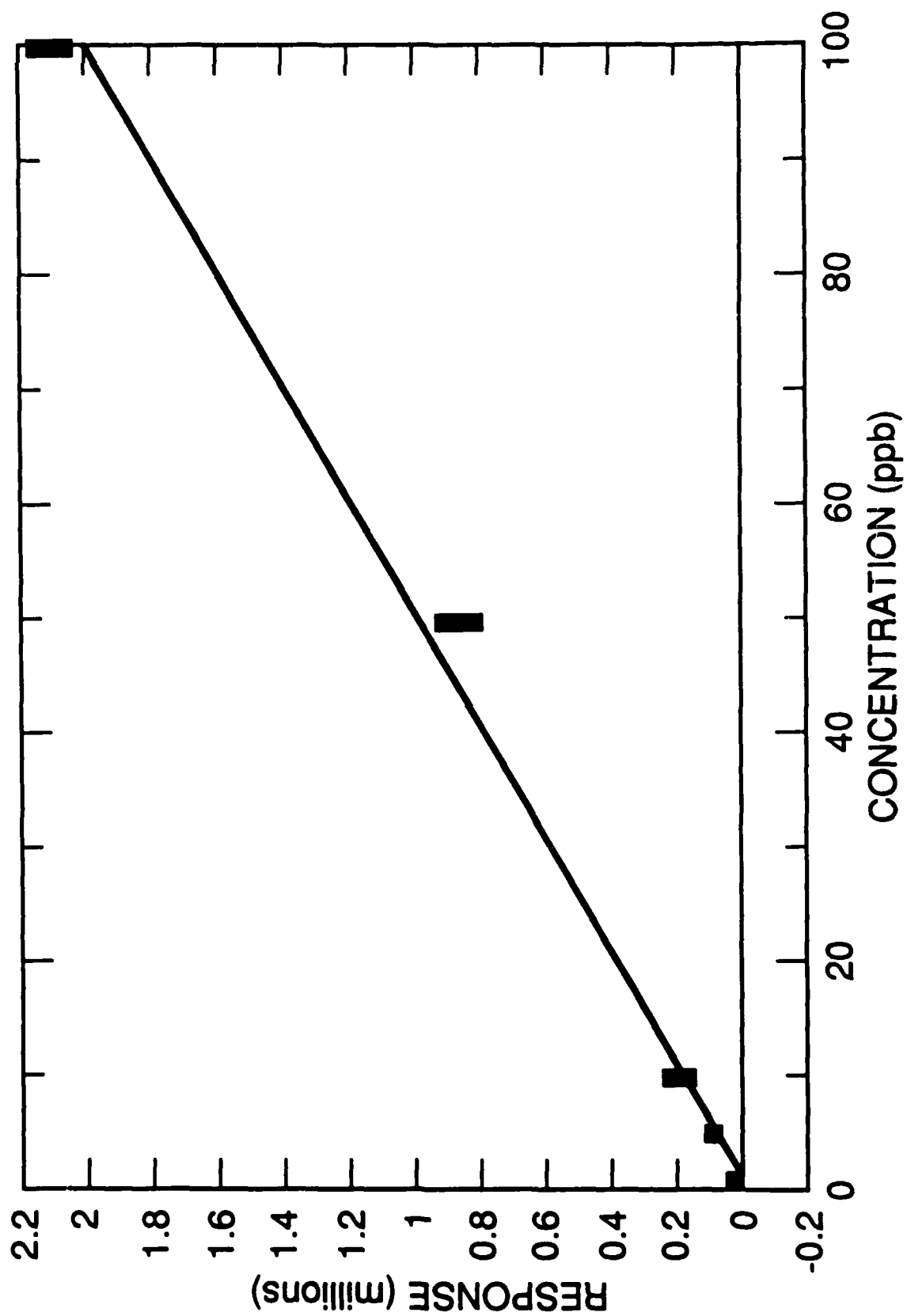


Figure 16. Benzene in Water by ITMS, Solution Purge

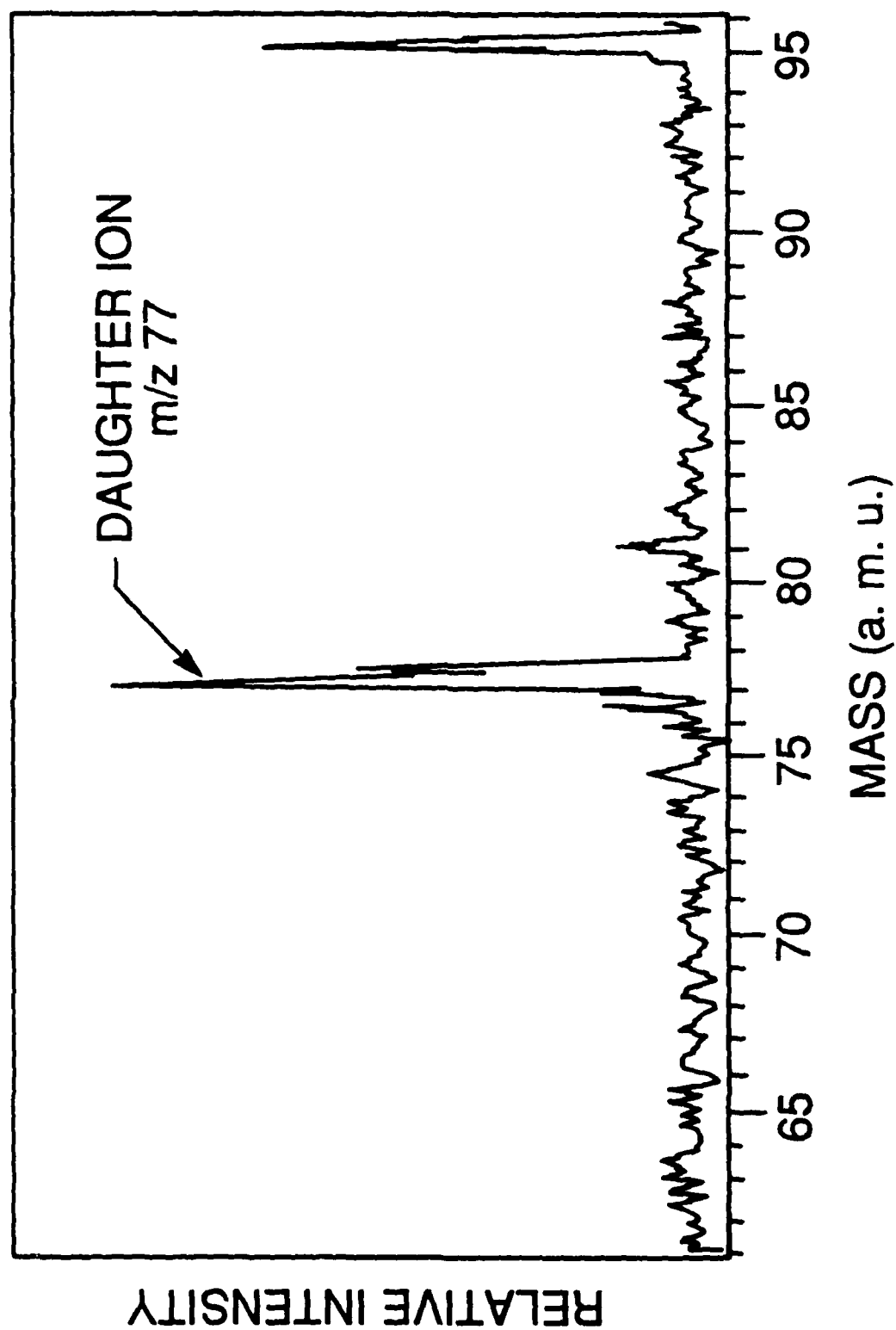


Figure 17. MS/MS of Benzene in Water at 500 ppt - ITMS (m/z 79 \rightarrow m/z 77)

As shown in Figure 18, the complete purge experiment may be conducted in a few minutes. Using a flow of about 100 mL/min, it was found that collecting data for two minutes was sufficient for the majority of the volatile compounds to be purged from water and to obtain good reproducibility. Figure 18 shows the purge profiles for four separate solutions of vinyl chloride in water, at levels of 2, 10, 20, and 40 ppb. The material was purged from each sample in a little over one minute, allowing all four samples to be run in twelve minutes. The ability to observe vinyl chloride at these levels is significant because of its high level of biological activity and the difficulty with which it is measured by conventional purge and trap methods.

Attempts were also made to use direct sampling ITMS for the analysis of formaldehyde in water. This highly volatile compound (gaseous at room temperature) was chosen for study because it is polar and it readily forms hydrates in water. This compound is typically difficult to determine by purge and trap techniques. Results with direct sampling ITMS indicate that only low ppm levels may be detected by direct purge from the aqueous solution. Ions were observed at m/z 45 and m/z 75 which appeared to track the concentration of formaldehyde in the water. These ions, which may have been formic acid and the hydrated formaldehyde dimer, purged very slowly from the water. Also, solutions of diethyl-N-nitrosoamine were investigated, but detection limits appear to be in the low ppm range. Although not attempted in these brief studies, it may be possible to determine formaldehyde and diethyl-N-nitrosamine by thermal desorption from sorbent beds, as described in the section on Additional ITMS Studies, below.

Complex mixtures in water were also tested. In one study, a series of fossil-derived fuels in water, including an unleaded gasoline, a jet fuel and a diesel fuel, were examined using direct sampling ITMS. Solutions containing about 200 ppb of total organics were purged directly into the ITMS under water chemical ionization conditions. The resulting spectra exhibited ions corresponding to the $(M + H)^+$ ions from the alkyl aromatics, which are preferentially protonated relative to the aliphatic hydrocarbons in these mixtures, as shown in Figure 19 for an aqueous solution of unleaded gasoline. The selective detection of alkyl aromatics allowed the three types of fuels to be qualitatively distinguished, with the unleaded gasoline exhibiting the highest concentration of aromatics, followed by the jet fuel, and then the diesel fuel. This suggests that water chemical ionization combined with direct sampling ITMS could be useful for rapidly characterizing a fuel spill in the environment, and perhaps could even be used to establish the source of the spill.

It was also determined that volatiles in oils could be purged for direct analyses by ITMS. Figure 20 shows a mixture of four halocarbons, tetrachloroethylene (m/z 166), trichloroethylene (m/z 134), methylene chloride (m/z 183), and chloroform (not shown) at a total concentration of 1000 ppm in used crankcase oil. As expected, the purge process takes longer than in water, but a distinct signal is observed for the halocarbons allowing them to be quantitatively determined. This suggests that direct sampling ITMS could be applicable to the detection of volatiles in oily samples, such as wastes and oil-contaminated soils.

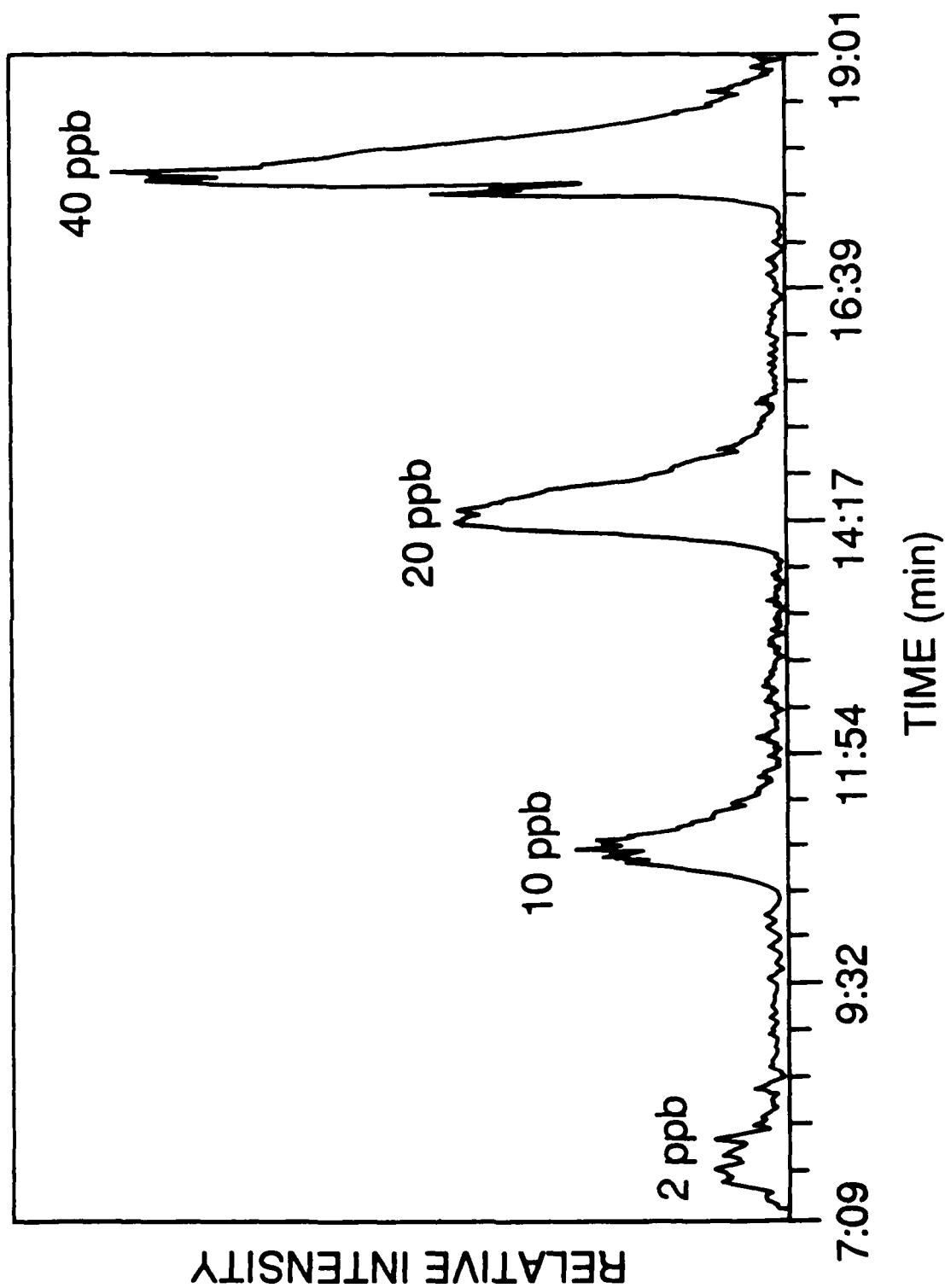


Figure 18. Solution Purge Profiles of Aqueous Vinyl Chloride Standards (ppb = ng/mL)

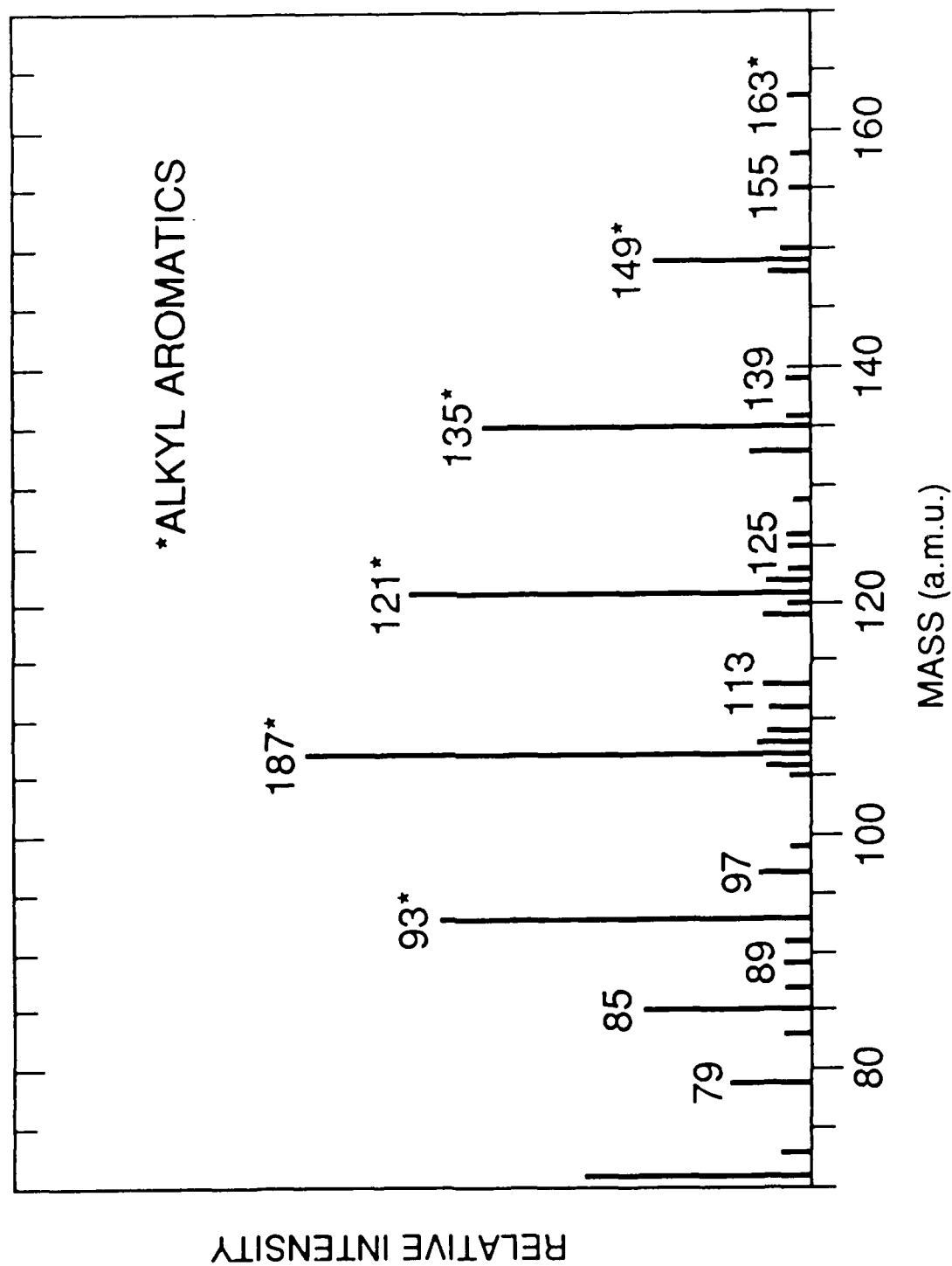


Figure 19. MS of Unleaded Gasoline in Water (200 ppb Total Organic) - Solution Purge, ITMS Water Chemical Ionization

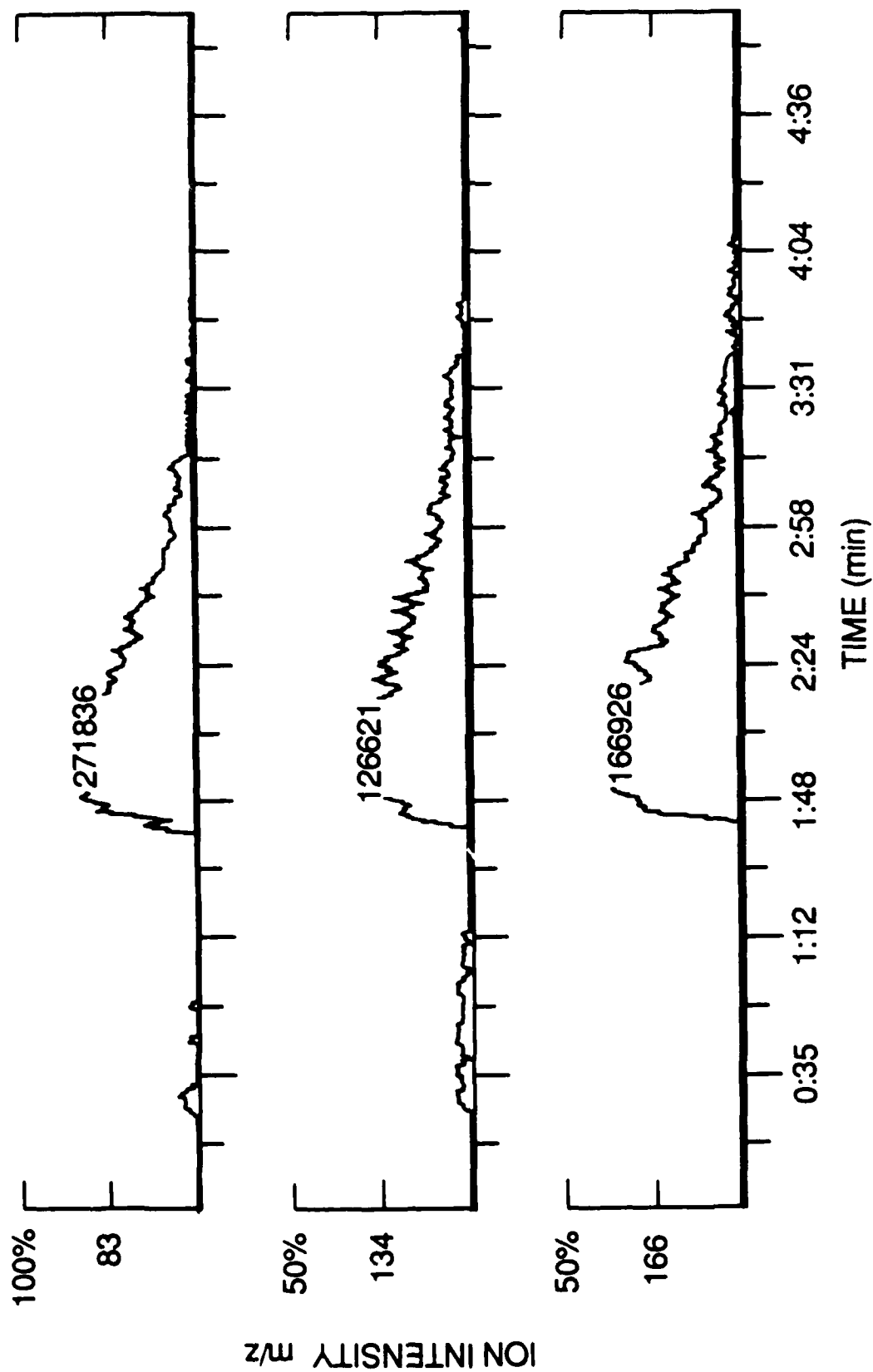


Figure 20. Purge Profile of Used Motor Oil Spiked with 1000 ppm of Chlorocarbons, Oil Purge, ITMS Water Chemical Ionization

Volatiles in Soils

The direct purge of volatile organics from soil samples was performed in a manner similar to that used for water samples. Typically a slurry was prepared by adding 15 mL of distilled in glass water to 5 grams of soil in a sealed 40 mL VOA vial. The solution was slowly stirred using a mini-stir bar in a closed VOA vial for a few minutes before analysis. The 40 mL vials were used in preference to the 25 mL vials used for aqueous samples because some sputtering occurs during the purging of the soil samples. The extra room in the 40 mL vial greatly reduces the chance of material being sputtered into the transfer line leading to the ITMS. Also, the purge rate was maintained at 20 mL/minute to decrease the possibility of sputtering. Soils investigated included clay, sand, and loam, and all were found to respond well to direct purge.

In parallel to a study performed in our Division for the Air Force, a series of soil samples contaminated with jet fuel were investigated by direct sampling ITMS. This gave an excellent opportunity to challenge the direct soil purge method using ITMS with conventional sample preparation and analysis techniques. For the direct sampling ITMS method, slurries of the soil samples were prepared by adding 15 mL of distilled in glass water to 5 grams of soil. These solutions were purged directly into the ITMS. In the conventional analysis method, the samples were extracted ultrasonically into a solvent, concentrated, and analyzed using a gas chromatograph equipped with a flame ionization detector.

Four soil samples were analyzed, including a sample below the detection limits of the GC method ($< 10 \mu\text{g/g}$), one at the detection limit of the GC method, a moderately contaminated sample, and a highly contaminated sample containing several ppm of JP-4. Figure 21 shows the spectrum obtained from the sample which contained JP-4 at the detection limit of the GC method. This spectrum was obtained under water chemical ionization conditions, which as explained previously, gives selective detection of alkylaromatics and would allow characterization of the type of fuel in the sample. Although absolute quantitation was not performed with the ITMS on these four contaminated soil samples, a good signal was observed for the sample below the detection limit of the GC, suggesting detection limits below $10 \mu\text{g/g}$. It should be emphasized, however, that the direct purge ITMS method not only appears to have detection limits at or slightly better than the GC method used, but also requires minimal sample preparation and no chromatographic separation. The total time required for sample preparation and analysis using direct purge ITMS is between 5 and 10 minutes, compared to the GC method which requires over 4 hours total time. As a result, time and cost savings could be substantial even when only a few samples need to be analyzed.

Additional ITMS Studies

A number of other scoping studies were conducted using the ITMS to investigate other uses of this instrument for environmental measurements, occupational exposure monitoring, and process monitoring. These studies are outlined briefly below.

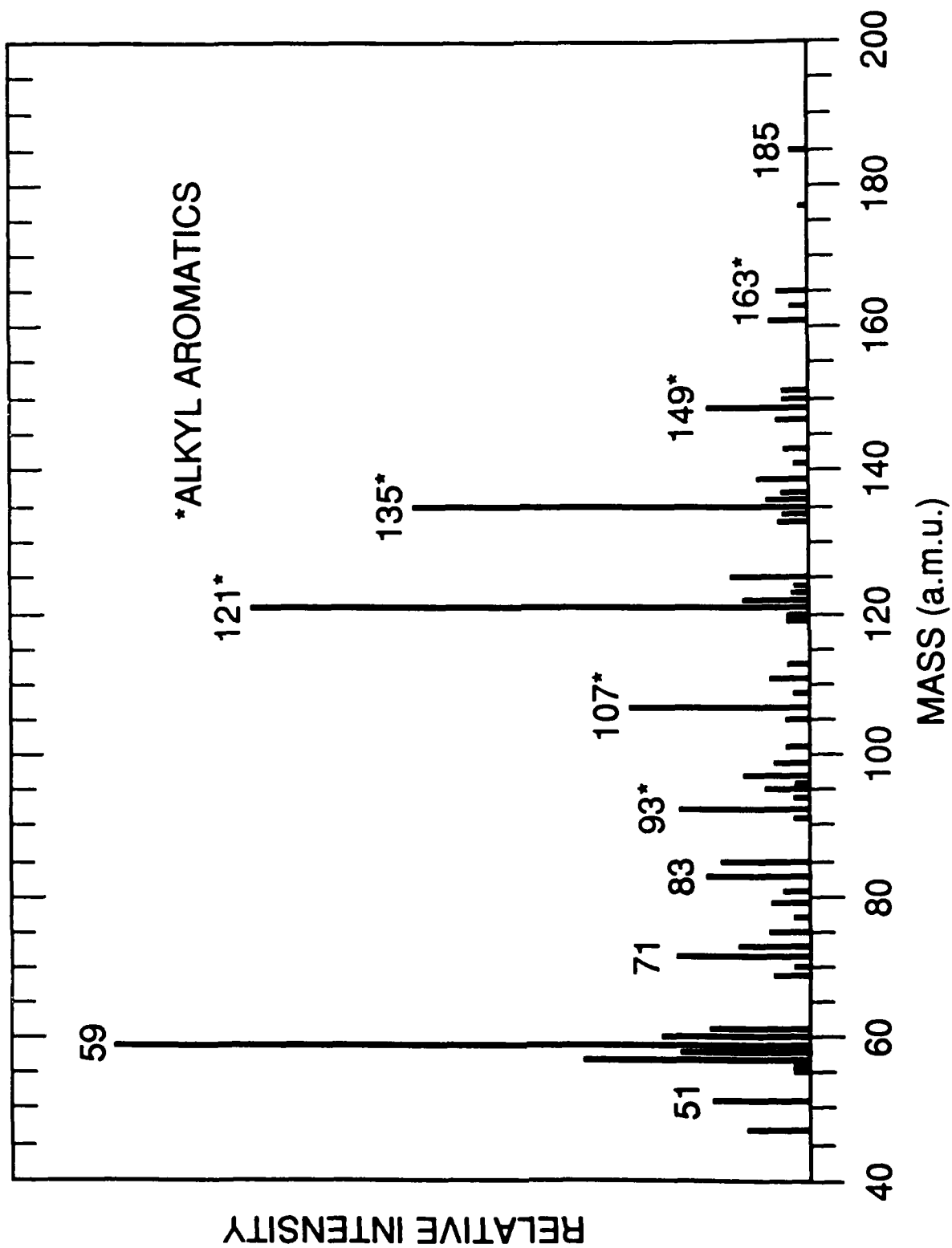


Figure 21. MS of Jet Fuel in Soil ($10 \mu\text{g/g}$) - Slurry Purge, ITMS Water Chemical Ionization

1. Thermal Desorption ITMS

In addition to thermal desorption of chemical agents and agent simulants as part of the OPMCD project mentioned earlier, thermal desorption was investigated as a means of analyzing semivolatile materials. In particular, it was of interest to investigate whether materials which would be sampled either from air or solutions could be thermally desorbed for analysis by ITMS with little or no sample preparation. Standards of several known carcinogens which are commonly found in tobacco smoke were first investigated. The materials were introduced onto Tenax traps and heated using a thermal desorber similar in design to those incorporated in the automated device made for the OPMCD project. The temperature used for the desorption process was based upon the known boiling points of the compounds, but did not exceed 325°C, the decomposition temperature of Tenax resin. The desorbed compounds were introduced through the open/split interface into the ITMS under a helium flow rate of 20 mL/min.

Semivolatile compounds with boiling points below 200°C, including dimethyl-N-nitrosamine, diethyl-N-nitrosamine, N-nitrosopyrrolidine, and ortho-toluidine, were easily detected at levels of 1 ng. Figure 22 shows the response of 10 ng of dimethyl-N-nitrosamine desorbed from Tenax. Isobutane was used as the chemical ionization reagent to form $(M + H)^+$ at m/z 75. This ion was then collisionally dissociated to form the ion at m/z 44, which is shown in the lower trace. As may be seen from the ion current for the m/z 44 ion, the detection limit is significantly below 1 ng. Two compounds with boiling points over 250°C, β -naphthylamine and 4-aminobiphenyl, had higher detection limits, but were readily observed at levels of 10 ng. Because these were just scoping studies, attempts were not made to establish absolute detection limits. However, it is believed that the detection limits for semivolatile compounds analyzed by thermal desorption ITMS could easily be reduced to the low picogram range. Direct thermal desorption ITMS was also investigated as a means of analyzing low levels of nicotine in ambient air by direct thermal desorption ITMS. Tenax traps were used to collect the smoke samples, and the traps were analyzed by direct thermal desorption into the ITMS as outlined above. A parallel experiment using conventional sampling with glass filter pads, extraction into solvent and analysis by gas chromatography, was run for comparison with the ITMS method. The results of these parallel studies are given in Table 1. Again, it should be noted that conditions for the ITMS study were not optimized due to the scoping nature of this experiment. However, the results are quite encouraging. Because of the higher sensitivity of the ITMS, the direct sampling ITMS method required 2 minutes of sampling compared to 30 to 90 minutes for the GC method. Further, the analysis time for the ITMS method was 5 minutes per sample, compared with 30 minutes for the GC method.

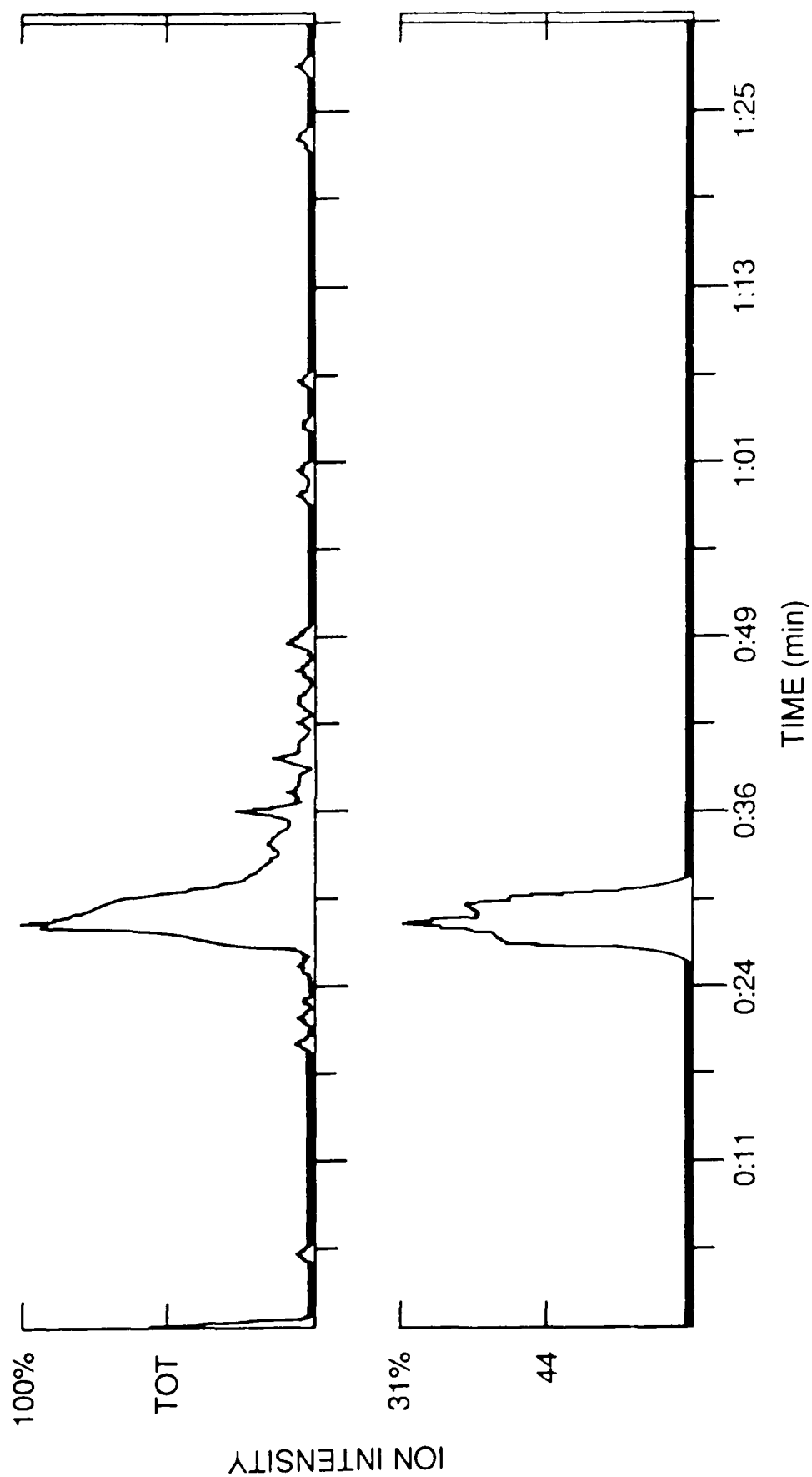


Figure 22. Thermal Desorption ITMS Profiles of Total Ion and Daughter Ion (m/z 75 \rightarrow m/z 44); Spectra from 10 ng of Dimethyl-n-Nitrosamine

Table 1

Nicotine in Ambient Air: Comparison of Data		
Sample	Thermal Desorption ITMS	Standard GC Method
Room Blank	$0.8 \pm 0.22 \mu\text{g}/\text{m}^3$	$0.45 \pm 0.13 \mu\text{g}/\text{m}^3$
1 Cigarette 1 puff/5 min	$27 \pm 3.6 \mu\text{g}/\text{m}^3$	$18 \pm 3.9 \mu\text{g}/\text{m}^3$
1 Cigarette 1 puff/1 min	$122 \pm 17.3 \mu\text{g}/\text{m}^3$	$123 \pm 25 \mu\text{g}/\text{m}^3$
1 Cigarette 1 puff/1 min + 1 Cigarette Continuous Smolder	$360 \pm 25.3 \mu\text{g}/\text{m}^3$	$260 \pm 50 \mu\text{g}/\text{m}^3$
1 Cigarette 1 puff/1 min	$141 \mu\text{g}/\text{m}^3$	$178 \mu\text{g}/\text{m}^3$
Sampling Time	2-5 minutes	30-90 minutes
Analysis Time Per Sample	5 minutes	30 minutes

Studies were also conducted to evaluate the use of direct thermal desorption ITMS for the rapid analysis of compounds in physiological media. In this study, nicotine was determined in urine from smokers and non-smokers. One (1) μL aliquots of urine were injected onto glass wool beds contained in glass tubes. The tubes were then inserted into the thermal desorption device and heated to 200-220°C. Isobutane was used as the chemical ionization reagent to produce $(\text{M} + \text{H})^+$ ions at m/z 163. These ions were collisionally dissociated and daughter ions at m/z 106 and 84 were monitored. Picograms of nicotine could be readily observed, allowing physiological levels of nicotine to be detected in 1 μL of urine from smokers. A typical MS/MS spectrum of nicotine in smoker's urine is shown in Figure 23. This figure illustrates the potential of direct sampling ITMS for analyzing trace components in urine, blood and possibly other physiological media. It is also believed that material from vegetation and other biological systems could also be analyzed with a minimum of sample preparation using direct thermal desorption ITMS.

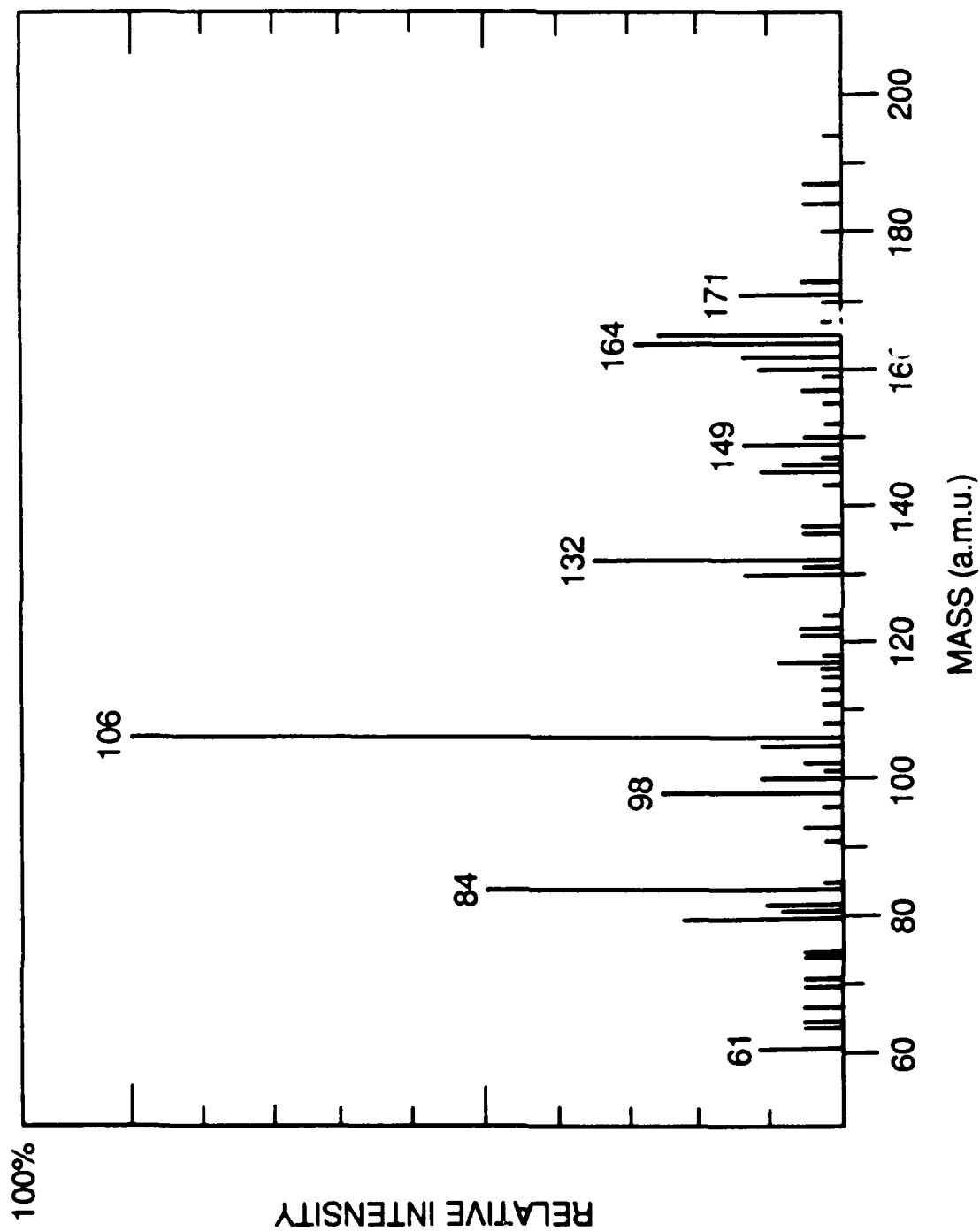


Figure 23. MS/MS of Nicotine in Smoker's Urine (1 μ L of Urine Injected into Thermal Desorber) - Isobutane Chemical Ionization, ITMS

2. Direct Air Sampling into the ITMS

We have also performed a few studies to determine if air could be sampled directly using ITMS without an intermediate trapping step. Figure 24 illustrates the response for a drop of a mixture of benzene, toluene, and xylene which was introduced into air about 15 feet from the ITMS. A small sampling pump was attached to the ITMS transfer line and introduced a small flow of air into the ITMS. The detection limits were not established, but the results indicate that direct sampling might be feasible.

3. Direct-Monitoring of Bioprocesses

Volatile materials in biological media and bioreactors have been successfully monitored by direct sampling ITMS. The first study involved the detection of part-per-million levels of octane in cell culture media. The second involved the real-time detection of organics produced by microbial degradation of coal. In both studies, direct purge of the volatile materials into the ITMS was found to be a successful means of monitoring the targeted compounds.

CONCLUSIONS

Results to date have shown that both glow discharge mass spectrometry and direct sampling ITMS have great potential for the rapid analysis of compounds in environmental matrices. Both techniques minimize the *time required* for both sample preparation and analysis. This time savings results in considerable cost savings as well. Further, the potential exists for using these technologies in the field as a rapid screening method. A portable instrument could be used, for example, in support of site remediation projects where quick analytical results are highly desirable. Other potential uses in the field would be for real-time monitoring on streams or wells, or in more fundamental studies involving environmental mapping of waste transport.

Although both glow discharge mass spectrometry and direct sampling mass spectrometry have demonstrated potential for the rapid analysis of compounds, it is useful to compare and contrast their strengths and weaknesses. In Table 2, some of these features are outlined.

Glow Discharge ionization on a single quadrupole mass spectrometer represents an inexpensive method for the rapid detection of targeted compounds. It could also be readily adapted for use as a real-time monitor for air or process streams. The glow discharge source can be easily fitted onto any quadrupole instrument, some of which sell for less than \$40K (although high sensitivity instruments are more expensive, around \$140K). The glow discharge source interfaced to a quadrupole mass analyzer is rugged and has low power requirements. It has potential for being portable.

The main disadvantage of glow discharge with a quadrupole mass analyzer is that it has more limited applicability for the analysis of complex mixtures. This arises because of possible interferences from compounds in the sample matrix. In many instances, however, this would not be a severe problem. However, a tandem mass spectrometer (MS/MS)

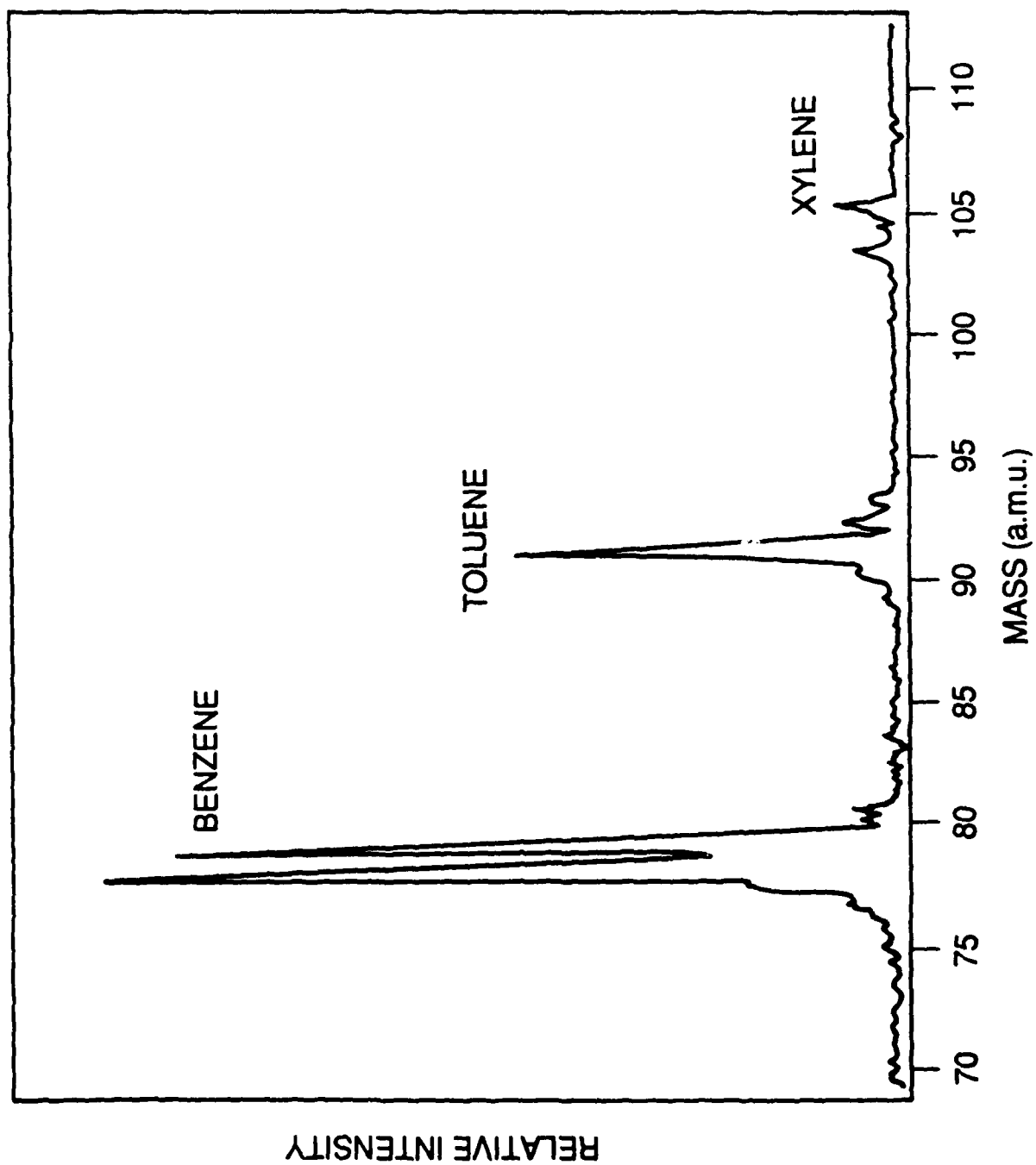


Figure 24. Aromatics in Ambient Air - Ion Trap Direct Air Sampling

could be employed with the glow discharge source if interferences were encountered. For example, the glow discharge source could be readily interfaced to a triple quadrupole mass spectrometer. This instrument is very expensive (> \$350K), however, and is much more difficult to operate and maintain and has far less potential for being portable. Further, the relatively low transmission of ions through all three sets of analyzer rods result in loss of overall sensitivity.

Direct sampling ITMS can be more readily applied to the analysis of mixtures because of its ability to obtain MS/MS spectra. This feature can minimize or eliminate the need for chromatographic steps greatly increasing the speed of analysis. This instrument has detection limits 10 to 100 times better than other MS/MS devices, allowing it to detect picograms (10^{-12} grams) or even lower amounts of material. It also has more potential of being made into a field portable device than conventional MS/MS instruments. The instrument is rugged, reliable, and simple to use and maintain. As the instrument is now designed, it is fairly large. However, it could easily be made smaller so that it would be van portable.

It should be noted that a number of trapped ion devices are commercially available at the present time. Two instruments related to the ITMS which are also produced by Finnigan are the Ion Trap Detector (ITD) and the newer ITS40. The ITD is essentially a single stage analyzer which is not capable of MS/MS experiments. It also cannot store or eject ions, reducing its sensitivity and selectivity relative to the ITMS. The ITD also does not perform CI reactions. The ITS40 is essentially an ITD which has the ability to store ions as they are formed which gives it added sensitivity over the ITD. It cannot perform MS/MS experiments, however, and cannot be used to manipulate ions to enhance selectivity as may be done on the ITMS. One other trapped ion device, Fourier transform mass spectrometry (FTMS), is perhaps even more versatile than the ITMS, but it is large and not readily suited for direct sampling because, unlike the ITMS, it operates under high vacuum conditions ($< 10^{-6}$ torr). In addition to the Finnigan ITMS, other similar instruments based on trapped ion techniques are being developed and might prove to be applicable to the types of studies described in this report. Some of these instruments are quite small and would be quite portable. We are monitoring the development of these instruments as information becomes available.

As illustrated in Figure 25, a variety of sampling options are available for the detection of materials from a variety of sample matrices using either direct sampling ITMS or GDMS. For example, direct introduction of air into the instrument could be used as an air, stack, or process monitor. Materials purged from water or soil samples may be directly introduced into either instrument. Samples adsorbed on traps (charcoal, resin, or even glass wool) may be thermally desorbed into either instrument. This approach could be used for air or liquid samples. Finally, liquid samples such as water, urine and other media from biota, may be injected onto sorbents and thermally desorbed into either instrument. Thus, the wide range of sample introduction methods which may be used with either the ITMS or GDMS gives these technologies broad applicability to a variety of analytical situations.

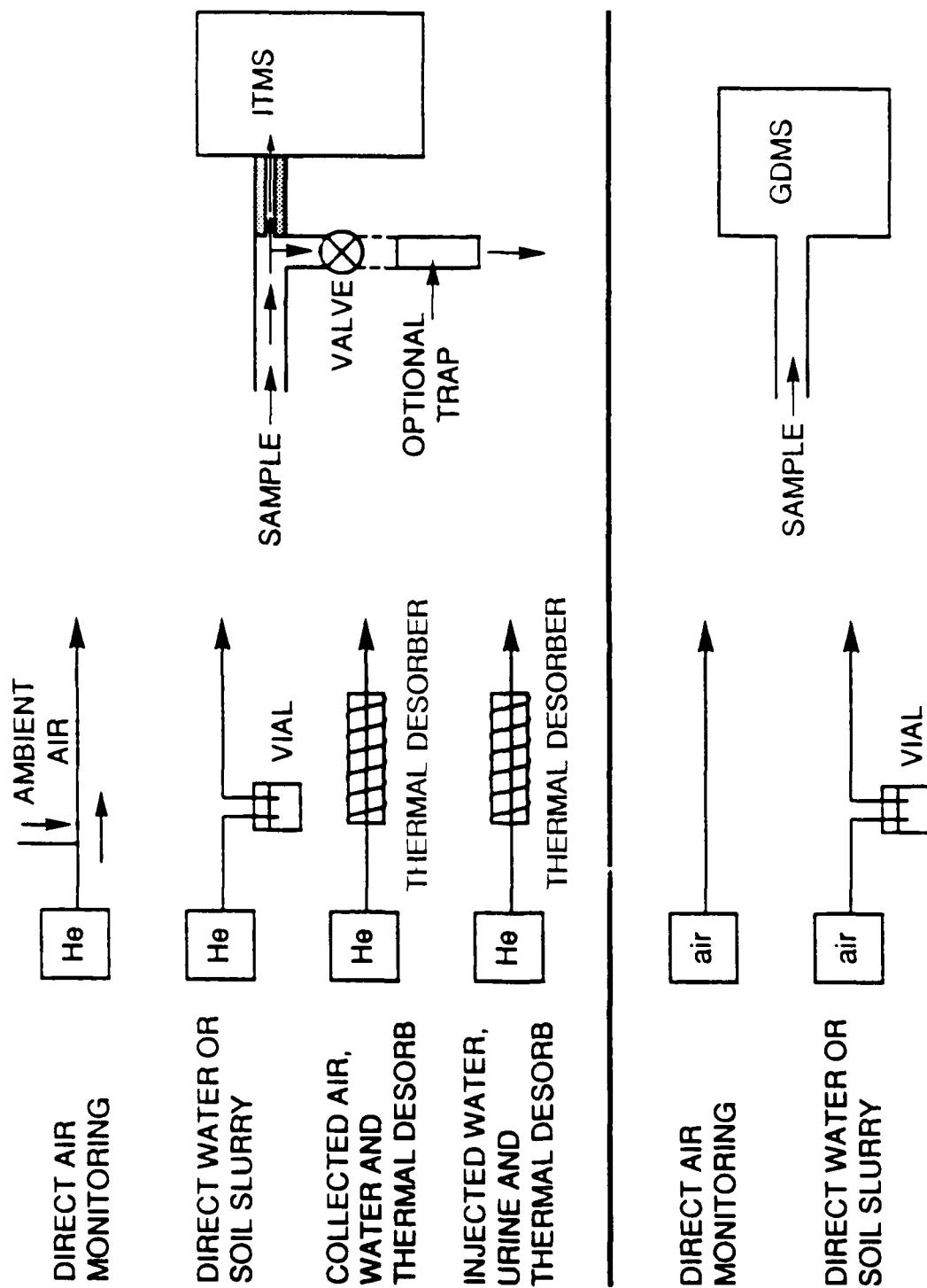


Figure 25. Direct Sampling ITMS and GDMS Methods Studied

Table 2

Comparison of Glow Discharge and Direct Sampling ITMS		
Feature	Glow Discharge Quadrupole ^a	Direct Sampling ITMS
Positive ions	yes	yes
Negative ions	yes	yes ^b
Chemical ionization	yes	yes
Mass range (upper)	2000	650
MS/MS capability	no ^a	yes
Detection limits	pg ^d	fg to pg
Size	Moderate	Small to Moderate ^e
Portability	Fair	Excellent to Good
Ruggedness	Good	Very Good ^f
Cost	\$150K	\$230K ^c
Power Requirements	Excellent	Very Good
Mixture analysis	Fair ^a	Very Good
Targeted Compound	Good	Excellent
Reliability	Very Good	Excellent ^f

^a Only single quadrupole instrument is represented. Glow discharge source could be interfaced to triple quadrupole, allowing it to perform MS/MS experiments, thus making it more amenable to mixture analysis; however cost would increase to \$350K. Portability, reliability, and detection limits would be considerably reduced relative to ITMS.

^b Potentially can detect negative ions, although presently cannot generate electron capture negative ion spectra without external ionization source.

^c Should be under \$100K when commercially produced.

^d These detection limits were established with the older Finnigan 3200 system outfitted with a glow discharge source. Undoubtedly, lower detection limits (by a factor of 10 to 100) will be possible with the newer instrument presently being assembled.

^e Has high potential for being made considerably smaller than quadrupole instrument, making it much more portable; present commercial instrument is moderate in size.

^f ITMS has fewer parts than quadrupole instrument to maintain and nothing to lose alignment when moved or bumped.

To date, direct sampling ITMS has been able to analyze all of the matrices that can be analyzed by the glow discharge mass spectrometer. A current restriction of direct sampling ITMS is that it is not as easy to form negative ions in the ITMS at present. This arises from the inability to form a large population of low energy electrons in the ITMS, which is required for electron capture processes to occur. However, glow discharge has recently

been interfaced to an ITMS by other investigators here at ORNL, which allows negative ion spectra to be obtained readily for the ultratrace detection of explosives in air.

Table 3 shows the range of compounds tested to date on the GDMS and the ITMS in water, soil, resin traps, and other media. The detection limits listed are not absolute because in no case were conditions optimized for obtaining maximum sensitivity. Further studies on both the GDMS and ITMS will address issues of ultimate detection limits, as well as extending the studies to a wider range of compounds of interest to USATHAMA, including semivolatiles, and further investigation of organics in soils. Particular attention will be given to identifying interfering analytes and to developing routine operating procedures.

Table 3

Comparison of Detection Limits Determined to Date

Note: These are not lowest possible detection limits because in most cases the instruments have not been optimized.

Matrix/Compound	ITMS	GDMS
<u>Water</u>		
Benzene	< 1 ppb	< 8 ppb
Toluene	< 1 ppb	< 10 ppb
Xylene	< 1 ppb	< 10 ppb
Methylene Chloride	< 1 ppb	ND ^a
Chloroform	< 1 ppb	< 10 ppb
Trichloroethylene	< 1 ppb	< 5 ppb
Tetrachloroethylene	< 1 ppb	< 10 ppb
Dichloroethane	< 1 ppb	ND
Vinyl Chloride	< 1 ppb	ND
Bromomethane	< 1 ppb	ND
Phenol	ND	< 5 ppm
2,4-Dinitrotoluene	ND	^b
Formaldehyde	^b	ND
Fuels (jet, gasoline, diesel)	<< 100 ppb	ND
<u>Air/Sorbent Traps</u>		
DIMP	< 50 pg	ND
DMMP	< 50 pg	ND
Butyl Sulfide	< 50 pg	ND
VX (G analog)	< 50 pg	ND
GB	< 50 pg	ND
HD	< 50 pg	ND

^a ND = not determined.

^b Does not purge; could be achievable using thermal desorption.

Table 3 Cont'd

Comparison of Detection Limits Determined to Date

Note: These are not lowest possible detection limits because in most cases the instruments have not been optimized.

Matrix/Compound	ITMS	GDMS
<u>Water/Thermal Desorption</u>		
Dimethyl-N-nitrosamine	< 100 pg	ND
Diethyl-N-nitrosamine	< 100 pg	ND
N-nitrosopyrrolidine	< 100 pg	ND
o-Toluidine	< 100 pg	ND
β -Naphthylamine	< 100 pg	ND
4-Aminobiphenyl	< 100 pg	ND
Nicotine (in water)	1 pg	ND
Nicotine (in urine)	1 pg	ND
<u>Direct Air</u>		
DMMP	---	50 pptillion
Benzene	low ppb	ND
Toluene	low ppb	ND
Xylene	low ppb	ND
<u>Direct Purge Soils</u>		
Benzene	ND	low ppb
Jet Fuel in Soil	< 10 μ g/g	ND
<u>Chlorocarbons in Oil</u>		
Chloroform	< 200 ppb	ND
Trichloroethylene	< 200 ppb	ND
Tetrachloroethylene	< 200 ppb	ND
Methylenechloride	< 200 ppb	ND

APPENDIX I

Lack of Fit Parameters for Calibration Curves

Calibration Curve	Lack of Fit Ratios		
	Model With Intercept	Model Through Origin	Zero Intercept
Benzene in Water (GDMS)	-5.92	-2.85	20.12
Critical 95% F ratios	5.99	5.14	5.59
Benzene in Soil (GDMS)	3.21	0.41	0.16
Critical 95% F ratios	3.71	3.48	4.67
TCE in Water (GDMS)	-3.99	-2.61	87.85
Critical 95% F ratios	5.12	4.26	4.96
Benzene in Water (ITMS)	54.38	46.15	2.17
Critical 95% F ratios	3.29	3.06	4.41
Toluene in Water (ITMS)	3.99	2.66	2.07
Critical 95% F ratios	4.46	4.07	4.96
TCE in Water (ITMS)	3.84	2.56	0.02
Critical 95% F ratios	4.46	4.07	4.96
PERC in Water (ITMS)	5.96	2.98	0.68
Critical 95% F ratios	5.99	5.14	5.59
Vinyl Chloride in Water (ITMS)	3.26	2.35	20.35
Critical 95% F ratios	3.71	3.48	4.67

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